The use of diamond-filled polymers as thermally conductive composites.

Morlidge, Christopher Patrick

THE USE OF DIAMOND-FILLED POLYMERS AS THERMALLY CONDUCTIVE COMPOSITES

by

Christopher Patrick Morlidge B.Eng (Hons)

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Department of Materials Engineering
University of Wales Swansea
Singleton Park
Swansea

SUMMARY

A need for a material that combines excellent thermal conductivity with high electrical resistivity has been identified in the electrical industry. As many materials currently exist that conduct both materials the investigation was carried out into a ceramic filled polymer. Diamond was chosen as the filling material due to its exceptionally high thermal conductivity.

Three polymer materials were investigated as matrices for this material. The materials used were silicone rubber, polyester and a paint based on poly vinyl chloride. A study of method of production and mixing was first carried out to find the best route to produce the composite by ensuring even dispersion and ease of application. Various examination techniques were employed to find the success of the different processes. These methods were calibrated and optimised. The best methods of mixing and choice of filling material was established.

Thermal conductivity tests carried out on the composite materials showed that there was a marked increase in the thermal conductivity of the materials. The strength and thermal expansion of the silicone rubber based material were also increased.

Acknowledgements

My thanks to the endless support provided by my supervisor Dr. Cris Arnold without whom this thesis would never have been finished, or even started. Thank you for the opportunity to prove I can do it.

Of course I couldn't list the contributors to this thesis without mentioning my parents Sylvia and Peter Morlidge. Without their constant encouragement and support none of this would have been possible. Thank you for everything.

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TABLE OF CONTENTS

CHAPTER 1 INTRODUCTION

The history of the semiconductor has been one of the constant drive to improve performance, speed and higher degrees of integration. To achieve ever higher degrees of circuit density, reductions in circuit size were needed to be made. These advances have the undesirable effect of increasing the heat build up caused by electrical resistance. A threshold is being foreseen at which stage the main barrier to the improvement of the electronic components will be the ability to conduct heat away rapidly enough. As this heat accumulates, the performance of the electronic component will be compromised and its design life reduced.

In plastic encapsulated devices this problem is already encountered and is traditionally overcome by using embedded heat sinks. Such heat sinks are expensive, and bulky, increasing the size of the component. In addition, the components need to be joined to the heat sink by a specialist compound that transmits heat efficiently. While the excellent coating ability and electrical insulative property of plastics make them ideal materials, their main drawback is their extremely low thermal conductivity. The actual heat-producing component is very small and so coating the component in a high thermally conductive material would allow the heat to diffuse over a wider areas and cause it to dissipate more rapidly.

One way of increasing the thermal conductivity of polymers is to produce composites where the largest component is the filler. These fillers are blended into the polymer matrix to modify and improve the properties of the overall material. Improvements in one property, however, often lead to concessions in another.

An interesting case study is the current filler that is widely used in semiconductor encapsulants, fused silica. Fused silica is an amorphous form of quartz. Commercially most large chips and small package devices are transfer moulded using a polymer composite consisting of 20 - 30 weight % (approximately 30 - 45 vol. %) epoxy resin and 70 - 80 wt. % (55 - 70 vol. %) fused silica. This composite has several advantages; it is relatively cheap, dimensionally stable (that is, it has a low co-efficient of thermal

expansion), high moisture resistance and superior stress and electrical characteristics. There are however, disadvantages to this material, namely the low thermal conductivity (0.5-1.0 W/mK), although even this low conductivity is approximately seven times that of the neat epoxy resin. Therefore although the fused silica improves many of the physical and certain thermal properties it does not sufficiently improve the thermal conductivity.

Ideally, the electronics industry would like a material with all the properties of a plastic but with a higher thermal conductivity. This would enable electronic devices to be coated to prevent damage from stray electrical charges, physical damage or over-heating. While a metallic filler would have many of the desirable characteristics the possible electrical conductance would lead to it being useless for this application. Formulators are seeking improvements by replacing present materials of low thermal conductivity with higher thermal conductivity fillers while maintaining other crucial mechanical properties at the current levels, if not improving upon them.

Some materials that are being investigated for this role are ceramics of higher thermal conductivity such as crystalline silica, silicone carbide (SiC), aluminium nitride (AlN), boron nitride (BN), beryllium oxide (BeO) and of course, diamond.

The aim of this project was to investigate and define the thermal, and to a lesser extent, the mechanical properties of this novel composite material. To this end materials with three generic types of base have been investigated, a silicone based flexible rubber, a polyester based resin and a polyvinyl chloride based paint. These three very different materials that were produced to find the best combination of characteristics in a material for possible use as a high thermal conductivity composite. These materials were first investigated to find the most suitable form of manufacture, as a method was needed that could produce samples with a uniform degree of filler dispersion and a minimum of porosity in the sample. This was a major section of the work as each material provided different difficulties in manufacture that had to be overcome to provide the highest possible quality of sample.

Once a sample of sufficient quality was produced a series of tests were carried out to measure the thermal conductivity and in the case of the polyvinyl chloride based paint, the amount of heat emitted.

CHAPTER 2 LITERATURE REVIEW

2.1 An Introduction to Composites

There is no universally accepted definition of a composite material. Definitions can vary widely depending on the technical nature of the source consulted. In everyday and dictionary usage the definition used is that a composite consists of various parts or elements. This is understandably a vague definition and so a more precise definition is needed. The best working definition of composite materials is given by Schwartz (1):

"A composite material is a material brought about by combining materials differing in composition of form on a macroscale for the purpose of obtaining specific characteristics and properties. The constituents retain their identity such that they can be physically identified and they exhibit an interface between one another."

Obviously this definition is unwieldy and still would need clarification as it could be argued by an engineer that this definition includes many materials that would not usually be thought of as composites. Examples of these are pre-coated and impregnated materials. However, further refinement would lead to an unwieldy and unusable definition.

The form of composite materials that will be studied in this report is that of ceramic particles embedded in a polymer matrix. In this case the polymer matrix will be the body constituent, this serves to enclose the filler and give it its bulk form. The filler material is the structural constituent; this determines the internal properties of the composite.

2.1.1 Particulate Filled Composite Materials

Particulate composites have an additive constituent that is essentially one- or two-dimensional and macroscopic. These composites differ therefore from other composite materials such as flake or fibre in that the filler is usually, randomly dispersed and the distribution cannot be controlled as it can in others. This leads to particulate materials being isotropic, as opposed to flake or fibre reinforced materials that will almost always, by their very nature, be anisotropic. These isotropic natures also allow them to be more

easily manufactured as there is not the necessity to produce uniform conditions and alignments on all products.

The reasons for adding particulate fillers vary enormously and revolve around tailoring the exact properties of a material to desired levels (2). It is possible to use fillers to alter the physical properties of a material. Most commonly these are used to reduce the cost of materials by acting as bulk fillers. The primary concern of these filling materials is that they are plentiful and cheap. Typically, materials such as talc and wood flour are used as they do not degrade the properties of the composite significantly, while still reducing the amount of body constituent material used.

The effect of using a filler material is generally to increase the stiffness of the composite. This increase in the stiffness is due to the increased resistance to flow of the material. The extended theory was developed by Guth (3). This theorem stated that the stiffness of composite Ec is given by:

$$E_c = E_m\left(1 + 2.5v_f + 14.1v_f^2\right)$$

Where Em is the matrix stiffness and vf is the filler volume fraction. It is also possible to increase the strength of polymers by incorporating certain filling materials. Unlike stiffness, wherein there is a direct relationship between the amount of filling material and the resultant stiffness, the strength of a material is dependent on the interfacial bond. If this bond is good then the strength will increase (4), if not then the filling will lead to a reduction in strength (5). Similarly, in a composite where there is good interfacial bonding this will lead to improvements in toughness (4). Because of this reduction in strength in materials where the interfacial bond is weak, it is desirable to use materials that simultaneously strengthen, toughen and stiffen a material. The most commonly used structural constituent materials are therefore calcium carbonate (6), carbon black, silica, talc and mica (7,8). Another property of plastics that can be desirable is the relative ease with which the materials can combust. Materials such as Aluminium Trihydrate are typically used as a fire retardant in polymeric materials.

It is possible to alter the thermal and magnetic properties of composites by adding filler materials such as metals and ceramics. The thermal possibilities are discussed elsewhere in this report. The magnetic properties of the polymeric materials can be greatly increased allowing plastics to be used, in advanced cases, in place of traditional applications of ferro-magnetic materials. Such an example is the replacement of ferrous materials with entirely polymeric based parts in advanced electric motors. An electrically conductive material may be produced by adding metal flakes or fibres to form conductive paths through the insulative matrix of the polymer (9). Density can also be altered by the addition of metals or of hollow glass spheres allowing the plastic to be tailored to its task.

The filling of a polymer does have disadvantages along with the benefits of the ability to tailor the properties of the materials to the desired specifications. It is harder to process filled polymers due to the higher melt viscosities and greater wear on equipment.

Many filled systems are initially compounded using intensive mixers such as twin-screw extruders. Then injection molding and extrusion is possible. A compromise between ensuring a good mix and thorough wetting without particle breakage is needed (10). Because of the increased viscosity when a material is filled it is desirable to use a material with a lower initial viscosity. For this reason thermosets are attractive for filled systems, but have the drawback that they are limited by the impossibility of melt processing them.

This study focusses on thermal behaviour, especially thermal conductivity via the use of a filler of high thermal conductivity (diamond particles). The effects of filling on thermal conductivity are described below.

2.2 Transmission of Heat

Heat is transmitted via one of three mechanisms; conduction, convection or radiation. This thesis is largely concerned with the conduction of heat and to a lesser degree the radiation of heat. Convection requires movement of molecules to transmit heat and as such is only present in gases and liquids. When fluids or gases are heated, they expand, causing a drop in their density. In accordance with Archimedes principle they then rise through a cooler medium. Convection is only considered in this report in an effort to minimise its effect.

2.2.1 Theory of Thermal Conductivity

Heat can be transmitted through a solid in two ways. The first is via electron charge cloud drift, analogous to electrical conduction. This method is directly linked to the presence of free electrons, therefore the higher the electrical conductivity the higher the thermal conductivity. The second method of thermal conduction is that of energy being transmitted by lattice vibrational energy. These lattice vibrations are known as phonons.

Because of the very different natures of the two methods there is a great many implications for both the size and temperature dependence of the thermal conductivity, depending on which mechanism is most prevalent. The method for assessing the relative contributions of the two methods of conduction is by calculation of the Wiedmann-Franz ratio (11):

$$= \frac{\text{Thermal Conductivity} \times \text{Electrical Resistivity}}{\text{Temperature}} \left(\text{in } \mathrm{V}^2 K^{-2}\right)$$

A characteristic of materials that are dominated by electronic type conduction is that the Wiedmann-Franz ratio is near constant with varying temperature. Carbon-based materials, however, have wildly varying Wiedmann-Franz ratios. This variability is characteristic of

materials that have a largely phonon based thermal conduction mechanism. It is believed that this phonon conduction method is responsible for approximately 99% of the thermal conductivity of carbon-based materials (12).

The thermal conductivity of a phonon-dominated material, such as a carbon-based ceramic, can be described by the Debye equation (13):

$$K = bCvl$$

Where K is the thermal conductivity, b a constant, C the specific heat per unit volume, v the phonon velocity and l the mean free path of phonons.

The thermal conductivity of crystalline materials, such as diamond, is limited by the various scattering processes present. These processes have been understood and established for some time (14-16). At temperatures in the region of the Debye temperature (where the phonon wavelength is short) the main scattering mechanisms for phonons are their interaction with impurity atoms and their interaction with other phonons. This is only true for crystalline materials considered as an unbroken whole however, and does not take into account the effect of the boundaries of the material.

In composites there are obvious differences in that there are two phases present and the effect that a mixture of properties brings to the composite. There is a much higher degree of scattering as phonons propagate through a boundary that separates one phase from another than could ever come from impurities in the lattice. Because of the parallels between the two methods of transmission, phonon transport is often seen as analogous to that of sound transmission. This has led to a theory being suggested that this scattering can be predicted using the acoustic mismatch of the media. A series of experiments were performed to find if this acoustic mismatch theory could be proved (17). It was suggested that phonons incident at an interface between the two media will be refracted into the second medium and that some reflection can occur at the boundary. The theory suggested that this reflection was increased if there was a greater degree of difference between the sound velocities and the materials density, examples of which are shown in Table 2.1 (18).

Table 2.1: Values of sound velocities and densities for a variety of materials.

Material	Mean Sound Velocity (10^3 m s^{-1})	Density (10^3 kg m^{-3})
Epoxy	1.9	1.21
Soda – Glass	3.6	2.49
Quartz	4.4	2.65
Aluminium	6.4	2.7
Corundum	7.0	3.99
Diamond	13.4	3.52

It can be seen from this table that the values for diamond are significantly different to that of the epoxy resin. The theory of acoustic mismatch therefore predicts that there will be a greater degree of resistance to thermal flow through a diamond filled epoxy compound due to its high mean sound velocity and density.

In a volume medium the wave speed takes the general form:

$$v = \sqrt{\frac{elastic\ property}{inertial\ property}} = \sqrt{\frac{B}{\rho}}$$

where B is the bulk modulus of the material and ρ is its density.

It has been stated (19) that there are two mechanisms involved in the scattering of phonons; collision with other phonons and collision with defects in the lattice, crystal boundaries or pores. These two contributions can be defined as:

$$\frac{1}{l} = \frac{1}{l_e} + \frac{1}{l_d}$$

Where l is again the mean free path of electrons, le is the phonon-phonon scattering path length and ld is the spacing of inhomogeneities, defects in the grain boundary, etc.

In highly crystalline carbon materials there are few defects and grain boundaries. This leads to $1/ld$ being relatively small. However, temperature has a marked effect on the thermal conductivity of the material. This is because as there is an increase from intermediate to high temperatures the phonon-phonon scattering length increases. The most significant factor in defining the phonon scattering is le. In addition, this factor is inversely proportional to temperature, thus causing the thermal conductivity to decrease. On the other hand at lower temperatures the specific heat rapidly decreases to zero despite an increase in the phonon-phonon scattering length, which aids thermal conduction.

To find the thermal conductivity of a material there are several methods available. It is obvious from previous published work done that there are two basic methods that are widely used in one form or another (20-22).

The first is that of using Fourier's law of steady-state heat conduction and relies on the sample having a known temperature gradient applied to it. Fourier's law can be expressed using the following equation:

$$q = -k(dT/dx)$$

where q is the heat flux (W/m2), k the thermal conductivity (W/mK), and (dT/dx) the temperature gradient.

The second method involves the use of a non-steady-state heat flux to find the thermal diffusivity. This is generally done with a pulsed laser as a heat source and can be expressed with relation to heat flux as follows:

$$q = -\alpha(dU/dx)$$

where α is the thermal diffusivity (m2/s), and (dU/dx) the energy gradient. This method doesn't give a direct result for the thermal conductivity for the sample in question and a relationship between the conductivity and the diffusivity is needed. The relationship between thermal conductivity and thermal diffusivity is most simply defined as:

$$\alpha = \frac{k}{\rho \times C_p}$$

where ρ is the density and Cp the heat capacity of the specimen. Therefore, it is necessary to additionally find these values for the sample in question.

The two methods are both widely used in the literature but it is clear that it is the former that is favoured due to its simplicity (20,21). This is because the former method involves the measurement only of the immediate physical dimensions, such as weight, diameter and the temperature at the interface of the samples interfaces. The latter method, however, involves far more complex measurements of the sample density and heat capacity. This extra complication introduces the possibility of a greater degree of experimental error. The equipment necessary to find the thermal diffusivity is also prohibitively expensive and therefore not widely available, making it difficult to recreate others results.

2.2.2 Theory of Thermal Radiation

Heat can be also transmitted in the form of an electromagnetic wave. This means that it is considerably harder to measure the loss due to radiation than conduction. When radiated heat is incident on a surface a percentage is absorbed and the remainder is reflected. This absorbed energy causes an increase in vibrational or translational kinetic energy of the atoms or molecules; this increase of internal energy is usually apparent as an increase in temperature. It is important to note that all frequencies of the electromagnetic spectrum cause such an effect when they are absorbed. However, the waves emitted by heated objects are in a very specific wavelength range, it is in this range that most heat is carried. This is because most atoms at room temperature vibrate at about the frequency 10^{14} Hz. Therefore, a wave of frequency in the region of 10^{14} Hz would cause resonance in most materials at room temperature and would therefore be more efficient at transferring this electromagnetic wave energy to other atomic structures.

Waves in the region 10^{14} Hz are called infrared and are both radiated and absorbed by bodies at normal temperatures. Infrared radiation is emitted when thermal agitation causes changes in the vibrational and rotational energy states of molecules.

There are several ways of calculating heat lost as radiation. These either rely on calculating the heat lost from a source placed in such a situation so that the amount of heat lost through conduction or convection is minimal and known or an infra-red image is captured of the object in question.

In the case of the infrared image fairly accurate readings of the temperature of the surface of the material can be taken due to the strong variation of the wavelengths emitted with temperature. That is the infrared region can be split into regions, as indicated in Table 2.2 (23):

Table 2.2 Values for the infrared region of the spectrum.

	Near	Intermediate	Far
$\lambda/10^{-6}$ m	0.8-3	3-10	10-(1000)
ν/Hz	4×10^{14}	$4 \times 10^{14} - 3 \times 10^{13}$	3×10^{13}

Where the near region corresponds to temperatures of several thousands of degrees (as emitted by the sun) down to wavelengths of approximately 400 μm that is emitted by objects at room temperatures. However the equipment needed to take such readings is exorbitantly expensive and problems can be caused by the effect that different surfaces and surface finishes have on the wavelengths that are emitted. This is illustrated by the Stefan-Boltzmann equation (24):

$$E = \sigma e T^4$$

where, T is the source temperature in Kelvin, σ is Stefan's constant (5.6697×10^{-11} kW m^{-2} K^{-4}), e is emissivity; a constant and E is the total energy of all wavelengths radiated per second per square metre by a full radiator at temperature T, in kWm^{-2}.

The reflective and emissive power of various materials is defined by the emissivity. This emissivity stretches from an ideal black body (that is, a perfect absorber of incident heat radiation and a perfect emitter of all internal energy.) with a value of e as 1.0, to a perfectly reflective surface that emits no heat radiation with an emissivity of 0. All real bodies are in fact 'grey' bodies with emissivities somewhere in-between.

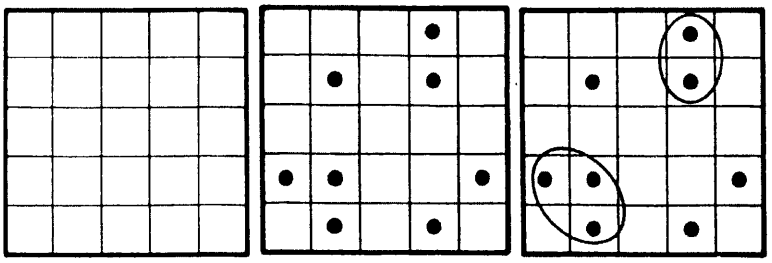
2.3 Thermal Conductivity In Particulate Composites

A theoretical basis for prediction of the effect different levels of filler loading will have on the properties of the material is needed. The foremost theory put forward is that of percolation theory (25). This theory has been modified repeatedly since its inception but remains the basis for all following thoughts. This theory is based on the principle of forming connections between conducting particles. When particles of high thermal conductivity, k, are added to materials of high thermal resistivity to improve the overall thermal conductivity, success depends on the degree of connection. This will determine the effects of particle-filler loading. Whereas mechanical properties will depend mainly on the absolute amount of filler, conductive properties depend more on connections. Therefore it is this connectivity level that becomes the vital point that must be predicted.

2.3.1. Percolation Theory

This theory begins by imagining a large array of squares as shown below in Figure 2.1(a). This array is imagined to be so large that any effects from its boundaries are negligible. Although the lattice shown is not of significant size it demonstrates the principle. A certain fraction of squares is filled with a large dot whereas others are left empty, as shown in Figure 2.1(b). A cluster can now be defined as a group of neighbouring squares containing a dot. In Figure 2.1(c) these clusters have been encircled. For the purposes of this explanation, all occupied squares sharing a side are taken to be linked and part of a cluster. All sites within a cluster are therefore connected by one unbroken chain of nearest neighbour links from one occupied square to a neighbour square also occupied by a dot. Percolation theory is the study of these clusters, their numbers and their properties.

The nature of the dots is not considered at this stage. It could be assumed that these dots are mutually attracted or repelled; for the purposes of this explanation they are assumed not to interact in any way. This means that the chance of a square being occupied by a dot is entirely random; that is the chance of any square being occupied or not is completely independent of the occupation status of its neighbour.



a) b) c)

Figure 2.1 Definition of clusters.

The probability that a site is occupied is defined as p. Therefore, in a grid of size N squares, where N is a very large number, then it can be said that pN squares are occupied, and $(1-p)N$ of theses squares are empty.

Figure 2.2 shows a range of computer-generated grids showing a 60 x 60 square lattice with the probability that a site is occupied, p, ranging from 10% to 70%. It can be seen that for p of over 0.6 one cluster extends from the top of the grid to the bottom and from the left to the right of the sample. A non-scientific analogy is the manner in which water percolates through sand. The threshold at which a contiguous cluster is formed, extending between two opposite sides, is the basis of percolation theory. The probability at which this percolating cluster is formed is the critical concentration, pc.

The percolating network at or around pc is likely to form a complicated path connecting two opposing sides. It is obvious that there is not necessarily a simple shortest path formed by the network. As p increases above pc there will be a larger network and therefore more chance of a straight link being formed. At probabilities in the region of pc however there can be a long, complicated path as shown in Figure 2.3.

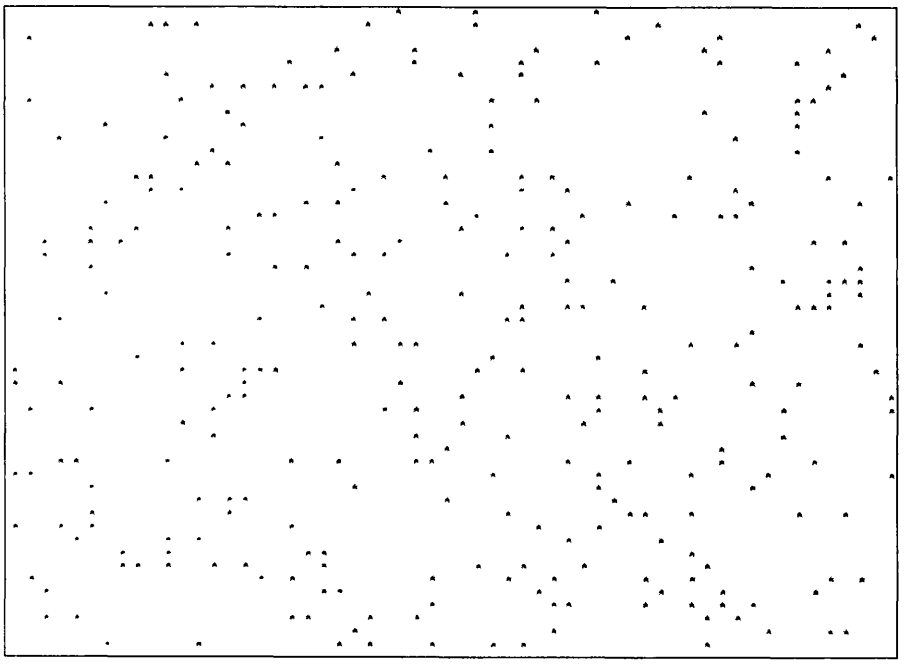


Figure 2.2(a). Example of percolation on a 60 x 60 square lattice, occupied squares are indicated by a star, p= 0.10.

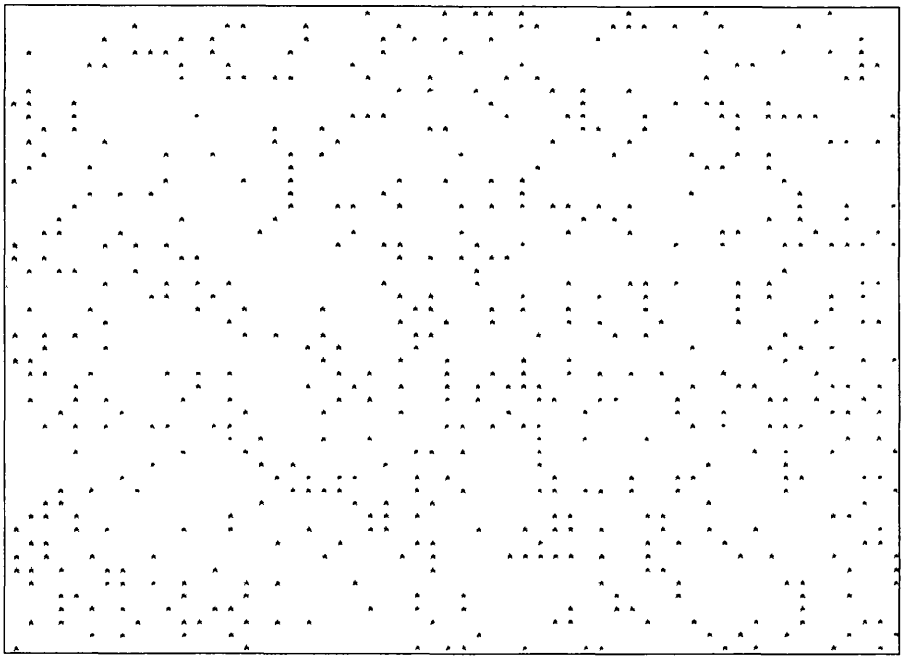


Figure 2.2(b) p=0.20.

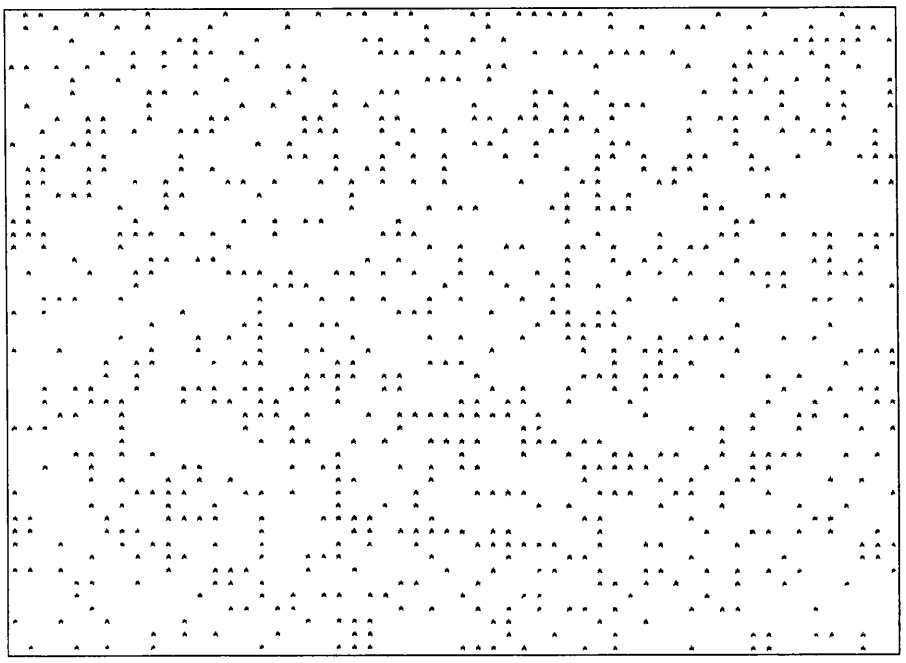


Figure 2.2(c) p=0.30.

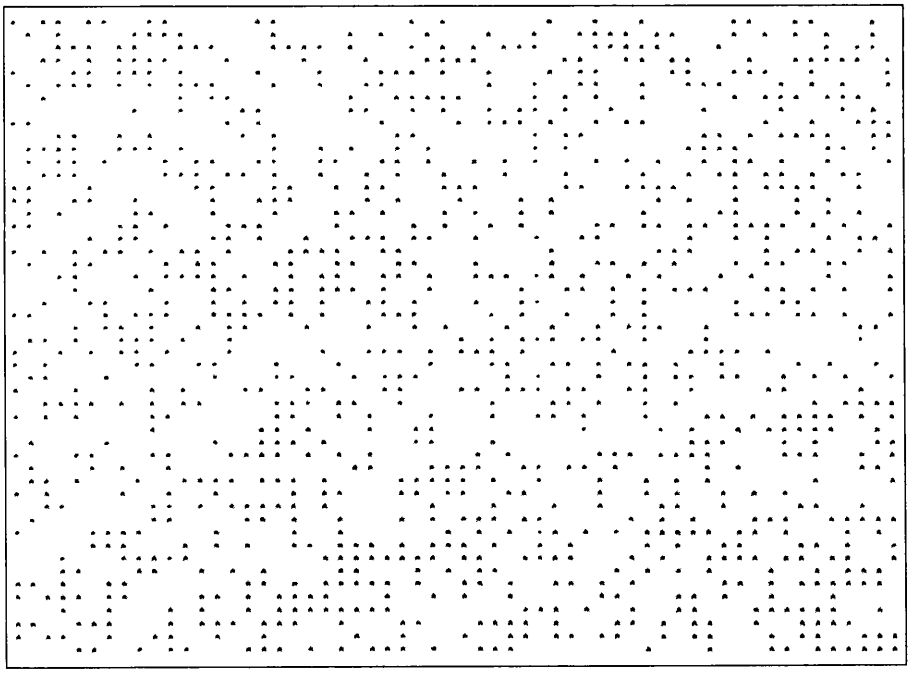


Figure 2.2(d) p=0.40.

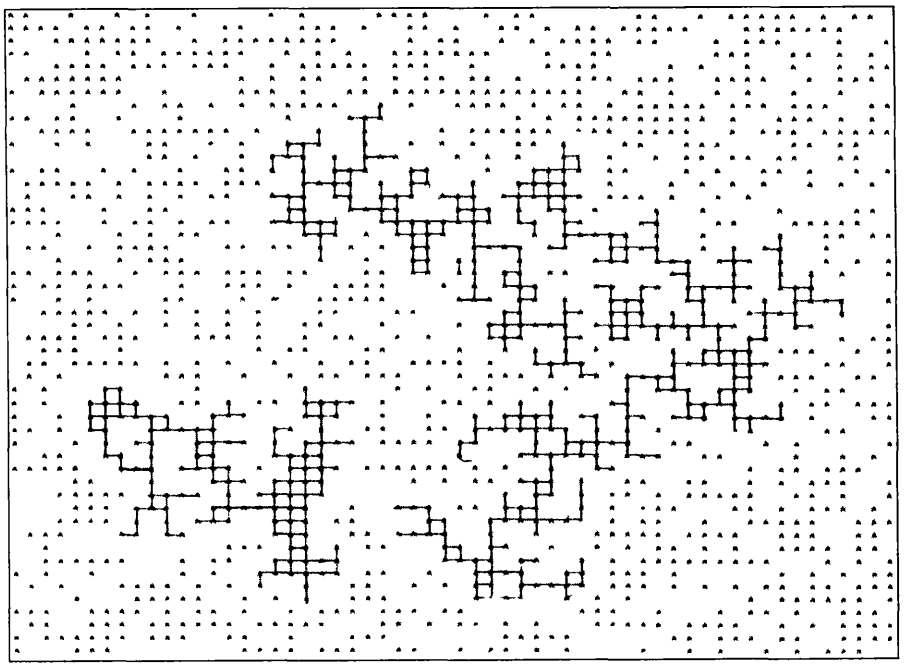


Figure 2.2(e) p=0.50. Largest clusters have been marked.

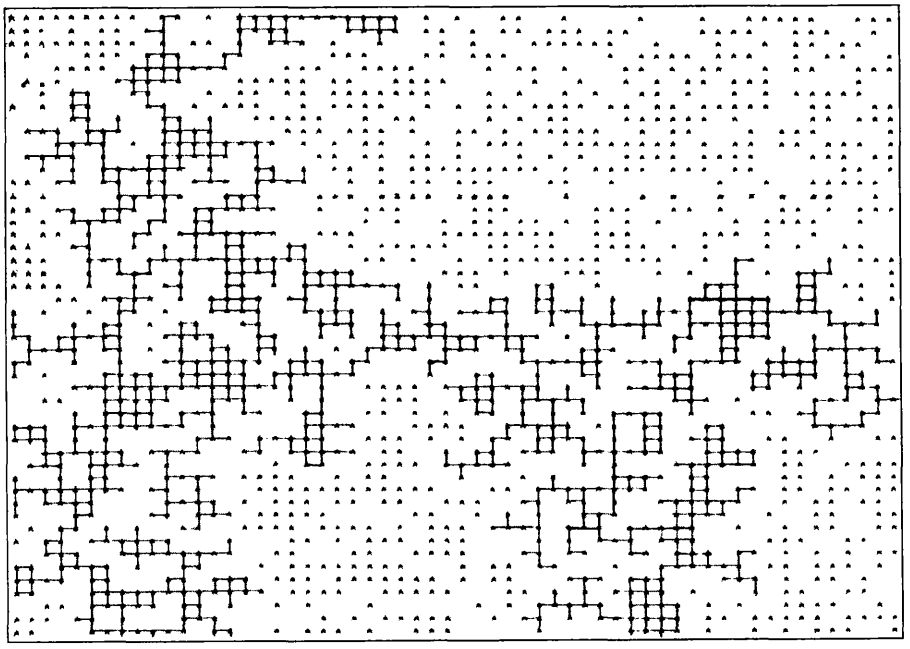


Figure 2.2(f) p=0.60. Largest cluster has been marked.

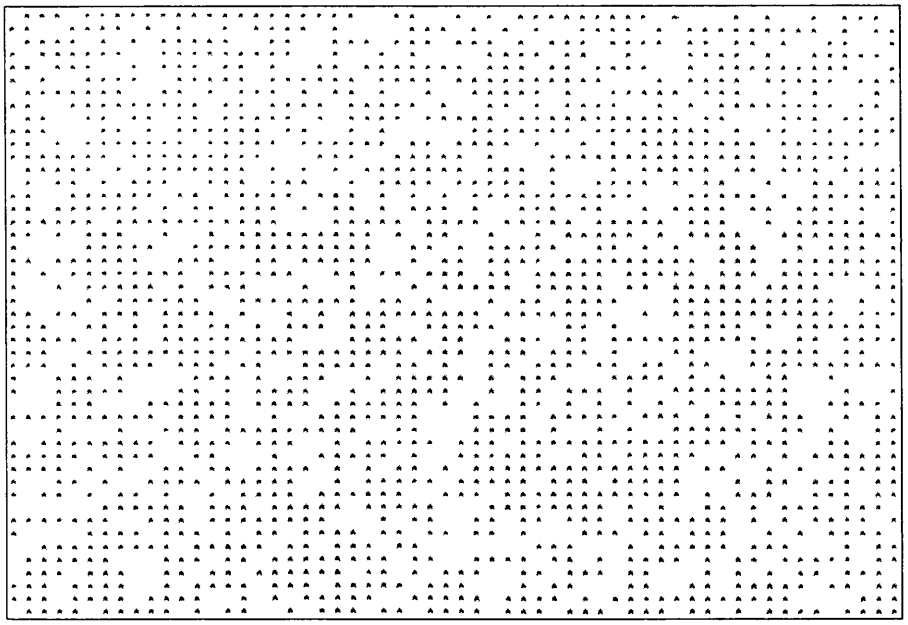


Figure 2.2(g) p=0.70.

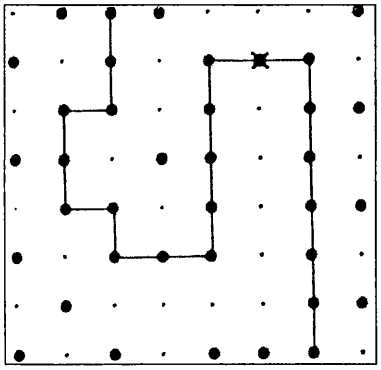


Figure 2.3. Example of the shortest path connecting the top and bottom of a small square lattice.

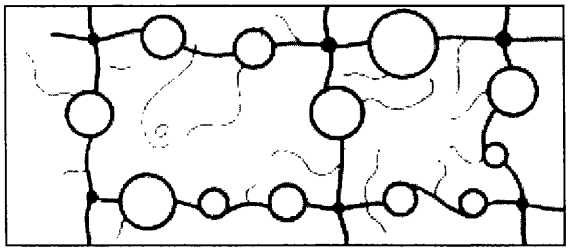


Figure 2.4. Schematic picture for the links (one dimensional chains), nodes (crossing points of the links) and blobs (dense regions with more than one connection between two points; shown as circular here). The thin lines are dead ends.

Historically percolation theory was first used by Flory and Stockmayer (25) who used it to describe how small branching molecules form larger and larger macromolecules if more and more chemical bonds are formed between the original molecules. This polymerisation process may lead to gelation, that is the formation of a network of chemical bonds spanning the whole system. In this example, the original molecules correspond to occupied squares, the macromolecules to clusters and the network to the percolating cluster.

It can be seen from Figure 2.2 that the infinite cluster has a very complicated structure. Here it should be clarified that a cluster is called infinite if it connects two opposing planes of a sample. It doesn't resemble a one-dimensional channel of occupied sites, but resembles more a network of roads with a series of dead ends. Figure 2.4 gives a schematic picture along these lines. It can be seen that the links meet at many crossing points, or nodes. It can also be seen that from these main roads there are many dead ends and offshoots of large areas of material. These 'dead ends' and offshoots, while increasing the total bulk of the percolating cluster don't actually help it to span the whole system. More simply, if we imagine an analogy to a material consisting of conducting filler in an insulating matrix, the occupied sites are conductive, the unoccupied insulative. If an electric voltage is applied to the top of the network in Figure 2.4 then the current will only be able to flow through the areas that directly connect the two sides. The dead ends, therefore, although they contribute conducting mass to the overall network, actually provide no additional conductivity. All conductivity travels via the connecting backbone.

Therefore, it is this conducting backbone that provides the limiting factor to the conductivity of the whole system.

The effect of the critical concentration on the electrical conductivity in the aforementioned model is shown in Figure 2.5. At low volume fractions, the conducting particles are isolated by the insulating matrix phase so that the composite system exhibits the high resistivity of the matrix. As the concentration of conductive filler particles increases a few random chains may form conducting paths through the sample, however these will have a negligible effect on the overall conductivity. It has been suggested (26) that this is because there will be an initial formation of bead-like chains which provide continuous conduction paths that mimic the behaviour of filaments of the conducting material. The transition from bead-like to fibre-like behaviour occurs at a critical volume fraction for which the average number of filler-filler contacts begins to exceed one. Further increases in the volume fraction concentration of the conducting filler cause a progressive increase in the average chain length of contacting filler elements, so that the behaviour rapidly tends towards the limiting behaviour of a continuous fibre system. The structure associated with the region intermediate between insulating and conducting behaviour is illustrated in Figure 2.5 by the closed circles that represent the contacting particles participating in chains of varying conduction path lengths. In this example the qualitative effect is illustrated by a filler ($\rho_f = 10^{-6}$ cm) in an insulating matrix ($\rho_f = 10^{16}$ cm).

A continued increase in the concentration of conducting filler causes an increase in the average number of contacts. Eventually the average number of contacts will exceed two so that chain branching occurs that gives rise to network formation. This second structural transition occurs at a 'saturation concentration'. Upon the onset of network formation, the multitude of continuous conduction paths causes a transition to behaviour dominated by the highly conducting filler material. The structure associated with the conducting plateau is illustrated in Figure 2.5 by the closed circles that represent contacting particles participating in a continuous network of conducting paths. A further increase in the concentration of conducting particles beyond the saturation concentration simply fills in the interstices of the network with additional conducting material so that the increased conductivity is proportional to the concentration of added filler.

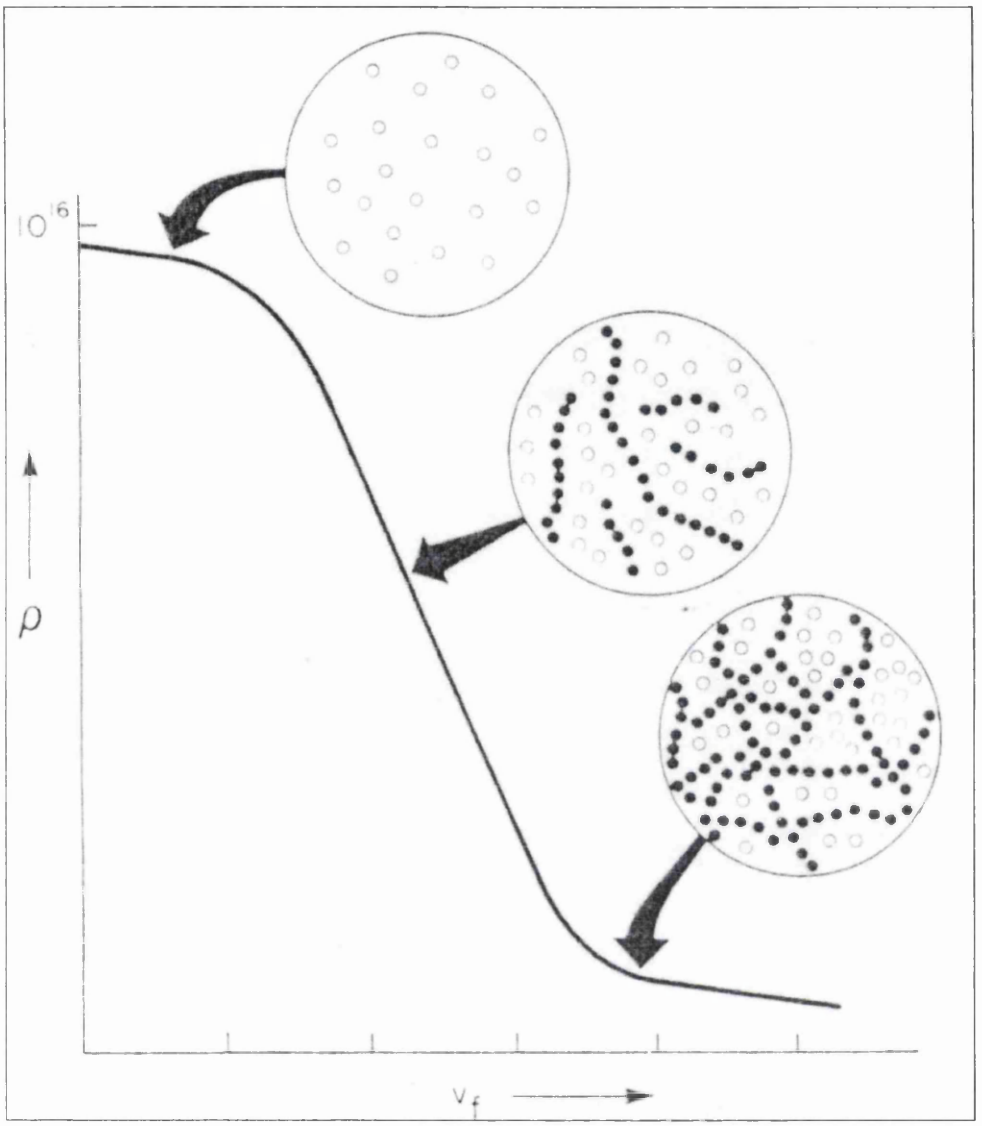


Figure 2.5 Illustration of chain formation in a particulate filled composite. Open circles indicate isolated particles; closed circles indicate contacting particles participating in chain formation.

A rigorous treatment of percolation processes is not available. The majority of the reported work is directed towards establishing empirical rules for specific systems, Particular emphasis has been given to developing expressions to predict the critical concentrations associated with percolation thresholds (27).

2.3.2. Theoretical Predictions of Thermal Conductivity

As was stated in the last section the majority of previous work has been directed towards the development of very specific formulae with little effort being made to find a general formula for the effect that filler concentration has on the conductivity of a composite material. Further, it is also apparent that very little work has been conducted on finding the thermal conductivity of composite materials and that therefore the equations have been adapted from the equations for electrical conductivity.

Dietrich Stauffer suggested that the general prediction of the conductivity of a material is almost impossible to calculate, but that there were certain basic rules (25). These rules were:

$$\Sigma \propto \left(p - p_c\right)^{\mu}$$

and

$$\Sigma \propto L^{-\beta}$$

where Σ is the electrical conductivity, L is the system size and μ and β are factors that vary with the situation they are being applied to. The first of these equations demonstrates that the electrical conductivity is proportional to a function of the probability that a site is filled minus the critical probability. That is, that at less than the percolation threshold, pc, there will be no electrical conductivity at all. The second equation states that the electrical conductivity is proportional to the size of the system.

Much work has been done on calculating the effect of sphericity on the electrical conductivity of composite materials. Unfortunately, this work does not translate well to the use in the field of thermal conductivity and it is only the basic equations that will be discussed here.

The earliest formula developed was the Rayleigh equation (28) that took the form:

$$k_c = k_m \frac{\left[\left(2+K_f\right)/\left(1-K_f\right)\right]-2v_f-0.525\left[\left(3-3K_f\right)/\left(4+3K_f\right)\right]v_f^{10/3}}{\left[\left(2+K_f\right)/\left(1-K_f\right)\right]+v_f-0.525\left[\left(3-3K_f\right)/\left(4+3K_f\right)\right]v_f^{10/3}}$$

In this equation *Kf* is *kf/km* where *kf* is the thermal conductivity of the structural constituent, *km* the thermal conductivity of the bulk constituent, *kc* is the thermal conductivity of the composite material and *vf* is the volume fraction of filler material. This equation assumes that the particles used are spherical particles of uniform size. It was developed by Rayleigh considering the case of uniform size spheres, and analysed the effect on the potential in the neighbourhood of a sphere by 248 of its closest neighbours (lying within the first fifteen shells around a central sphere). This equation was therefore based almost entirely on the electrical conductivity of materials. This theory was further advanced upon by Meredith and Tobias (29) who specifically adapted it for a more realistic treatment of composites. They derived the following formula:

$$k_c = k_m \left(A-2v_f+0.409Bv_f^{7/3}-2.133Cv_f^{10/3}\right) \Big/ \left(A+v_f+0.409Bv_f^{7/3}-0.906Cv_f^{10/3}\right)$$

Where *kc* is the thermal conductivity of the composite, *vf* is the volume fraction of the filler, and

$$A=\left(2+k_d\right)/\left(1-k_d\right),\ B=\left(6+3k_d\right)/\left(4+3k_d\right),\ C=\left(3-3k_d\right)/\left(4+3k_d\right),\ k_d=k_f/k_m$$

This formula is considered superior by many sources (21) and is preferentially used due to its consideration of the effects of high volume concentration of filler.

However, both the Rayleigh equation and Meredith and Tobias' modification only consider a dispersion of uniform, perfect spheres. Hashin and Shtrikman (30) developed a

formula for the thermal conductivity of a composite consisting of polydisperse spherical inclusions:

$$k_c = k_m\left[1+\frac{v_f}{\frac{1}{3}(1-v_f)+\frac{k_m}{k_f-k_m}}\right]$$

This expression was previously derived for a three-phase model by Kerner and also Christensen (31) demonstrating that these two models are equivalent. A comparison of the three models is shown in Figure 2.6.

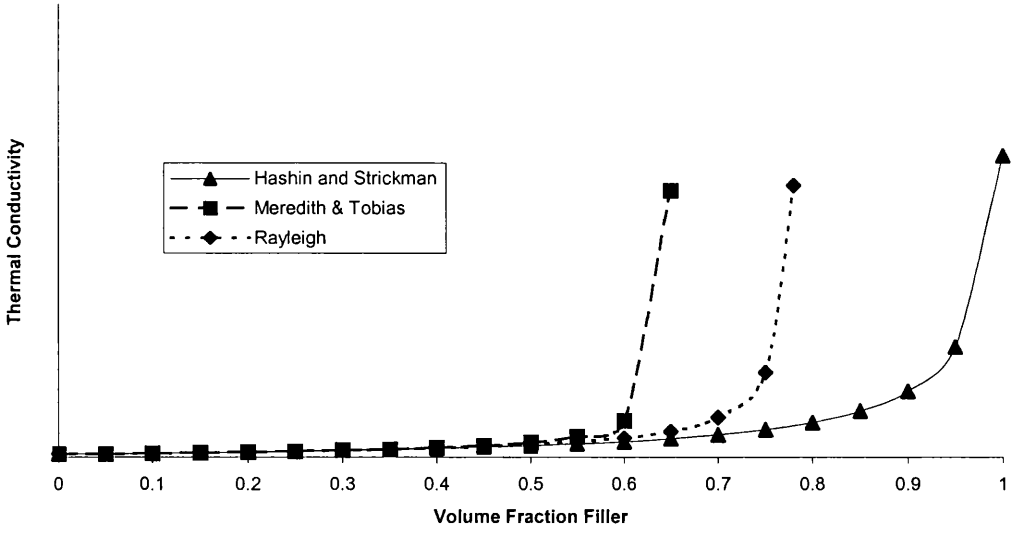


Figure 2.6 A comparison of various predictions of the thermal conductivities of composites.

In considering what factors could most effect the production of a very high thermally conductive composite, it is obvious that there are two factors. As can be seen the major difference between the three equation is that the Hashin and Shtrikman equation predicts that it is theoretically possible for there to be a composite consisting of 99.9% filler and almost no matrix. This clearly isn't possible as there must be a relatively even coating of matrix around the majority of the particles. Conversely, Meredith and Tobias and the

Rayleigh equations predict a sharp cut off in the rise of the thermal conductivity as they reach the point at which no more spheres can be close packed. Experimentally due to the impossibility of achieving a monodisperse mixture of filler the actual conductivity will actually be somewhere between the Meredith and Tobias equation and that of Hashin Shtrikman. Indeed this is confirmed by the research done by Bujard and Ansermat (32). However in this report and that of Garrett and Rosenberg's (21) it is pointed out that there is a significant difference between the conduction of electricity and that of phonons.

To prove these models, many experiments have been carried out and the formulae repeatedly confirmed. In almost all cases this proof was derived by the testing of electrical rather than thermal conductivity. There is a reluctance to accept these results for thermal conductivity due to the essential differences between the nature of conduction of electricity through metals and the transport of phonons through non-ionic materials. One paper that has investigated the plausibility of the Nielson model is that of Proctor and Solc (22). The Nielson model (33) is an adaptation of the Meredith and Tobias equation. It has been adapted to take into account the sphericity of the particles in the composite. Proctor and Solc performed a series of experiments in which the degree with which the thermal conductivity of the composite material varied with volume filler fraction of an epoxy resin/crystalline silica system was measured. The crystalline silica was used in the form of spherical particles of uniform size as far as was mechanically possible. This was to eliminate the uncertainty caused by having to calculate the varying sphericity from particle to particle. This is because the sphericity is largely a subjective value as the particles in question cannot be physically measured. These measurements of the thermal conductivity of the silica/epoxy composite largely agrees with the Nielsen and Meredith and Tobias models demonstrating some degree of correlation between theory and reality.

It is equally important that the awareness that as the conductivity of the filler begins to exceed approximately 100 times that of the matrix then the shape of the particle can become important. As the sphericity of the filler materials decreases and the particles become more irregular in shape this can affect the chance of particle-particle contact and the resultant conduction of heat along the material.

2.3.3. Effect of Relative Thermal Conductivity

It is obvious that the most important factor in the development of thermally conductive polymers is the effect of the volume fraction of the filler. The relative effect of the volume fraction and the filler's intrinsic conductivity is illustrated in Figure 2.7. The curves represent the theoretical relationships predicted by the Meredith and Tobias model for spherical fillers *kf/km* = 10, 100 and 1000 ratios.

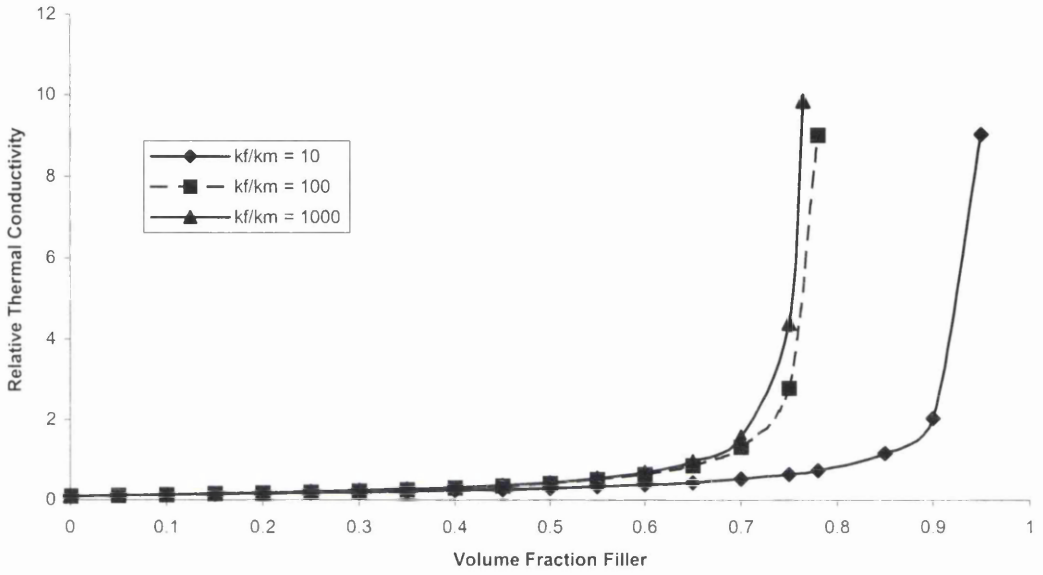


Figure 2.7 Relative Thermal Conductivity as a Function of Volume Fraction Filler.

It can be seen from Figure 2.7 that the filler's volume fraction has a significant impact on the conductivity. In the region from 0.7 - 0.8 there is a clear and sudden rise in the conductivity, this is the percolation threshold being reached as has been discussed in earlier sections and is due to the formation of a continuous network throughout the sample. Figure 2.7 also shows how increasing the ratio of filler to matrix conductivity from ten to a hundred leads to a dramatic increase in the overall conductivity of the composite material. However, it also implies that an increase of *kf/km* above about 20 will lead to insignificant increases in the thermal properties of the composite. This is borne out by a comparison of known thermal conductivities of various materials, as shown in Figure 2.8 (22):

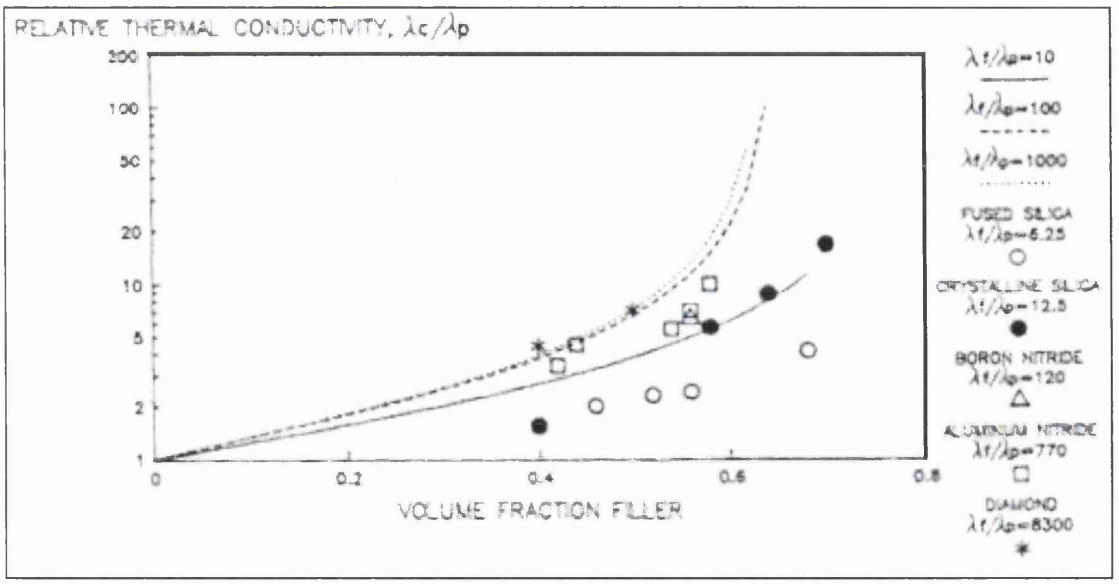


Figure 2.8 illustrates that the theory of ever decreasing gains for higher and higher ratios of filler is often applicable.

2.4 Commercially Available High Thermal Conductivity Products

Over the last few years the sector producing products designed specifically to be thermally conductive, but electrically insulative has increased from being essentially none to a handful of companies. These companies range from the large multinationals to individuals starting with this as their sole product.

These composites can be categorised into two basic types. There are those that are producing a product based on some form of silicone matrix and those that are using an epoxy resin as the body constituent. In general the silicone based products have been developed to provide a thermally conductive, flexible material that can be used to fill or seal gaps and as an adhesive in circumstances where a build up of heat would be undesirable. The epoxy products are designed for use in environments that require a more rigid, stronger material.

The field of silicone based highly thermally conductive products is led by G.E. Silicones and the Bergquist Company, both of whom produce extremely effective products. G.E. Silicones produces a one-part room temperature vulcanising product that has a thermal

conductivity of 1.68 W/mK (34). Bergquist company provides a silicone based sheet product that has been designed for aerospace and military applications, it is based on a silicone elastomer and is designed to provide the greatest degree of electrical insulation while maximising the heat conducted. This material has a thermal conductivity of 3.5 W/mK (35), more than five times the thermal conductivity of silicone alone.

Epoxy resins have been used quite successfully to produce a material that is capable of conducting heat but also acting as an electrical resistor. It is interesting to note that the most successful product in this category is not a mineral filler in a polymer matrix as with other materials being studied here. It is in fact a metal filled epoxy composite, named Arctic Silver (36). The structural constituent is in fact micronised silver at a concentration of 62-65 per cent by weight. This product has by far the largest thermal conductivity of all commercially available products at 7.5 W/mK, while maintaining negligent electrical conductivity. The closest competitor to this product is that produced by the company Epoxies, etc. with a thermal conductivity of 2.1 W/mK (37). This product is also based on an epoxy matrix with a mineral filler to boost its thermal properties.

2.5 Body Constituent Materials

Several theories have suggested that the effect of the body constituent material has further reaching consequences than at first thought. While the equations dealt with in a previous section would indicate that the thermal conductivity of the matrix is critically important they imply that it is limited to a linear effect. The equations state that as the conductivity of the matrix increases, the composite's conductivity will increase with it. However, it is important to acknowledge that the models have been designed with electrical conductivity in mind; this can lead to significant differences being overlooked. For example, there is the acoustic mismatch theory that states that materials that carry sound at differing rates will affect the passage of phonons. To study this effect three very different materials have been chosen to be studied. These are a silicone rubber, a polyester resin and a polyvinyl chloride based paint.

2.5.1 Silicone Rubber

Silicone rubbers were chosen for the first series of experiments due to their useful mechanical and thermal properties. These rubbers are one of the few in the family that have both a very low initial viscosity and a usefully large temperature operating range, making them more useful for applications where heat dissipation is important. There are a wide range of silicone elastomers, which are discussed in more detail below.

The general form of silicone polymers is the organo-siloxane polymers, indicated schematically below in Figure 2.9. The organic group 'R' is often as simple as a methyl group, but there are many variants. Crosslinking is required to form a material with reasonable strength, and this is achieved by producing oxygen bridges, as shown in Figure 2.10 (38).

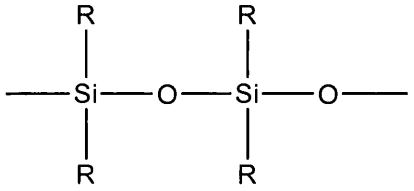


Figure 2.9 The basic repeating unit of silicone polymers

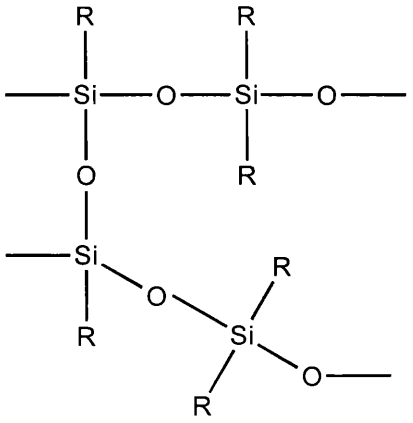


Figure 2.10 A typical crosslink in silicone polymers

The most widely used silicone elastomers are the room temperature vulcanising systems (RTV), which are generally produced as either one-part or two-part systems. The one-part systems are simplest to use, as they are normally applied by squeezing from a tube and then curing occurs over time in air. They are based on prepolymers of tetra-esters, which crosslink with water (which diffuses in from the environment), liberating acetic acid. This is shown schematically in Figure 2.11.

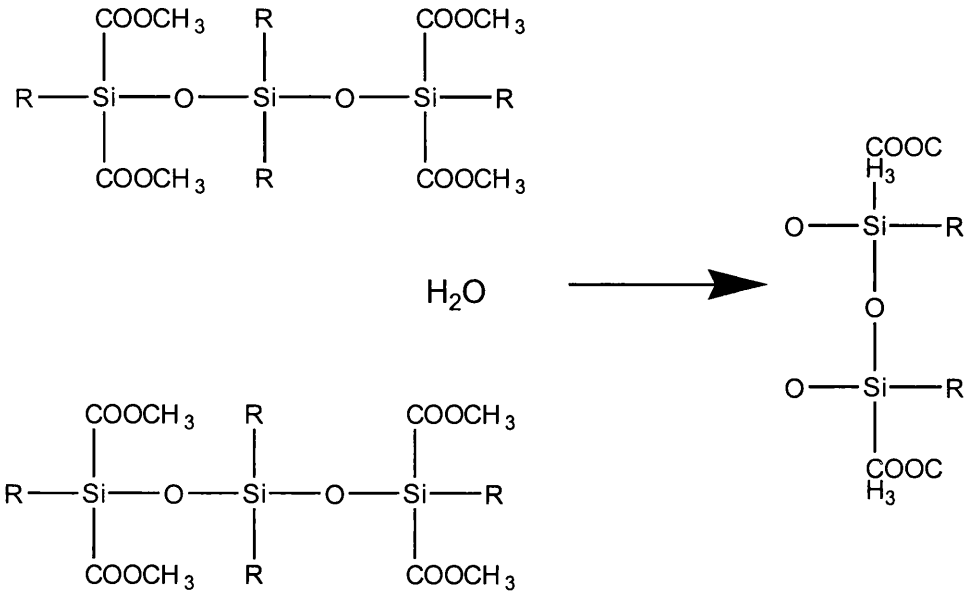


Figure 2.11 Curing system for one-part RTV elastomers.

2.5.2 Polyester

Polyesters of several diverse types are useful as polymers. However here only those resins in which the dibasic acid or the glycol, or both, contain double bonded carbon atoms are considered.

Much of the versatility of the reinforced polyester systems lies in the wide variation in resin composition and fabrication methods possible, allowing the properties of the product to be tailored to the requirements of the application. This variability is manifested in the large number of components used (38).

The unsaturated polyester can be broken down into three components, plus the peroxide hardener. The first of these components is that of the dibasic acids used. These acids provide the unsaturation in the resin and are usually maleic anhydride or fumaric acid. In

addition a saturated acid or anhydride is often used, such as phthalic anhydride or adipic, azelaic, or isophthalic acid. A higher proportion of unsaturation gives a more reactive resin, with improved stiffness at high temperatures, while more of the saturated components give less exothermic cures and less stiff resins, particularly if aliphatic resins are used.

The second component of the resin is a dihydric acid alcohol such as ethylene or propylene glycols which are most commonly used, but 1,3- and 2,3-butylene, diethylene, and dipropylene glycols are also common.

The final component is the monomer. Styrene is by far the most widely used monomer for these systems. Others often encountered are vinyl toluene, methyl methacrylate (leading to improved weatherability), diallyl phthalate (often preferred in moulding compounds), and triallyl cyanurate (imparting good heat resistance).

These components are mixed in a resin kettle and polymerised by step reaction to a molecular weight of 1000-5000, which is in the highly viscous liquid range. After cooling, the mixture is thinned down to a pourable liquid by the addition of the monomer. An inhibitor such as hydroquinone is then added to prevent premature polymerisation. When kept cool, the mixture is stable for months to years.

It is in this form it can added be added as resin to a hardener to form a solid. Cure is begun by adding an initiator, usually an organic peroxide, such as benzoyl peroxide, or a hydroperoxide. Typically, promoters or accelerators are used to promote the decomposition of the initiator at room temperature and, thus, rapid low temperature curing. Common accelerators are cobalt naphthenate or alkyl mercaptans. Cure takes place in two stages; the initial formation of a soft gel is followed by a rapid polymerisation.

Figure 2.12 Shows the basic repeating unit of polyethylene terephthalate, the most commonly found form of polyester.

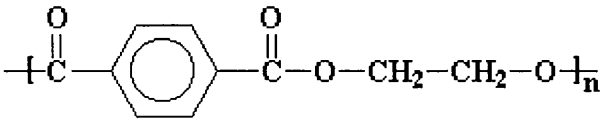


Figure 2.12 Basic repeating unit of polyethylene terephthalate.

2.5.3 Polyvinyl Chloride Based Paint

In its pure form, polyvinyl chloride (shown in Figure 2.13) is a colourless rigid material. It is widely used as a structural commodity plastic, and also for many paint systems, where it is partly dissolved in a solvent to form a 'plastisol'. It has a relatively high density and low softening point. Polyvinyl chloride has very limited solubility, with the most effective solvents being those which appear capable of some form of interaction with the polymer. It has been suggested (39) that polyvinyl chloride is a weak proton donor and effective solvents are proton acceptors. Thus the polymer is soluble at room temperature in oxygen-containing solvents such as ethers e.g. dioxan, tetrahydrofuran; ketones, e.g. cyclohexanone, methyl isobutyl ketone; and nitrocompounds e.g. nitrobenzene.

Polyvinyl chloride is unaffected by acids, alkalis and aqueous solutions; even strong oxidising agents such as chromic and nitric acids have little action. Uncompounded polyvinyl chloride has a relatively poor heat and light stability compared to other polymers (40). Exposure to temperatures above 70°C and/or ultraviolet light has a number of adverse affects on the properties of the polymer. The first physical manifestation of degradation is usually a change in colour. Thus when the initially colourless polymer is heated in air it turns in sequence, yellow, orange, brown, black. Further heating causes a general deterioration in mechanical and electrical properties. The commercial success of polyvinyl chloride has been very largely due to the discovery of stabilizers, the incorporation of which alleviates the effects of degradation and enables technologically useful materials to be made (41).

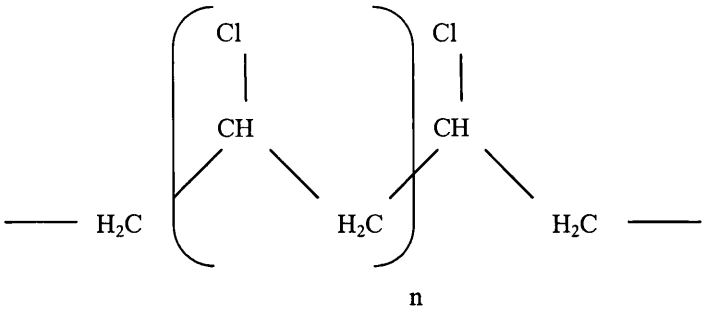


Figure 2.13 The basic repeating unit of polyvinyl chloride.

Polyvinyl chloride is better adapted as a paint by the addition of plasticisers. These reduce the glass transition temperature of the poly(vinyl chloride) and allow greater a greater degree of chain motion, resulting in a more flexible material (42). Most commonly plasticisers used are based on phthalates.

The logical extension of creating a more flexible paint using plasticisers is to use a system where the polyvinyl chloride is dissolved or dispersed in a mixture of the solvent and plasticiser to give the paint system. Applications of then include spray coating, roller and dip coating, especially useful for quite thick and flexible paint coatings.

CHAPTER 3 EXPERIMENTAL PROCEDURES

3.1 Thermal Conductivity Measurements

Thermal conductivity of samples was measured using an Armfield HT10X / HT11 system. This is illustrated schematically in Figure 3.1 below. It consists of a heated zone [1], attached to a thermally insulated brass cylinder, embedded in which are thermocouples T1, T2 and T3, spaced 15 mm apart. The sample is sandwiched between the heated zone and the cooled end [3]. The sample can either be in the form a cylinder (30 mm diameter, 25 mm long) embedded in a thermally insulated casing [2], or in the form of a thin section (less than 4 mm in thickness).

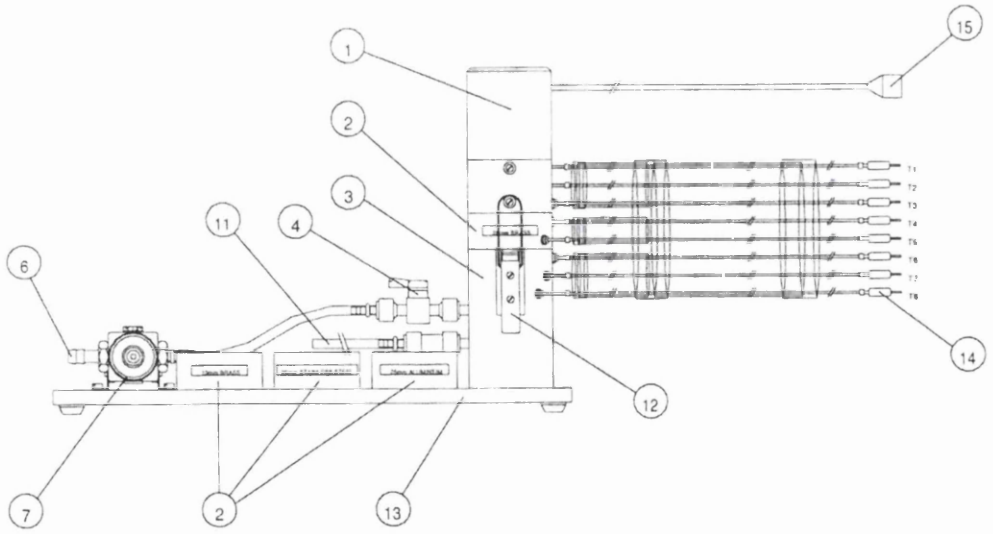


Figure 3.1 The Armfield Thermal Conductivity Measuring System

The cooled end [3] is a second brass cylinder, thermally insulated and water-cooled. The water-cooling was provided from mains water via a flow valve to ensure constant cooling. Three further thermocouples (T6, T7 and T8) are embedded in the cooled section. These thermocouples are also spaced 15mm apart.

The equipment operates on the basis of one-dimensional heat flow, according to the Fourier law of heat conduction as shown in the form below:

$$Q = kA\frac{\Delta T}{\Delta x}$$

Where Q is the heat flow (W), k is the thermal conductivity (W/mK), A the sample area (m^2), ΔT the temperature difference across the sample and Δx the sample thickness.

The heat flow is determined from the power input to the heater, which can be calculated from the voltage multiplied by the current. The sample area and thickness are easily measured. The temperature difference across the sample can be determined from the thermocouple readings as follows.

Initially, the thermocouples were calibrated to ensure they all gave readings that were in agreement with one another. This was done by allowing the equipment to stand and reach equilibrium at room temperature. No current was passed through the heating element and no water through the cooling section of the rig. The air temperature of the room in which the test equipment was set up was air conditioned and maintained at approximately 22 degrees centigrade. As a back up the ambient temperature was also recorded. It was possible from these readings to establish whether a thermocouple gave a high or low reading and adjust results accordingly. This procedure was performed several times to discover a trend. The results are shown below in Figure 3.2.

The reading of each thermocouple was then plotted against height (all were separated by 15 mm from each other, with T3 7.5mm above the sample, and T6 7.5mm below the sample). Such a plot is shown below in Figure 3.3.

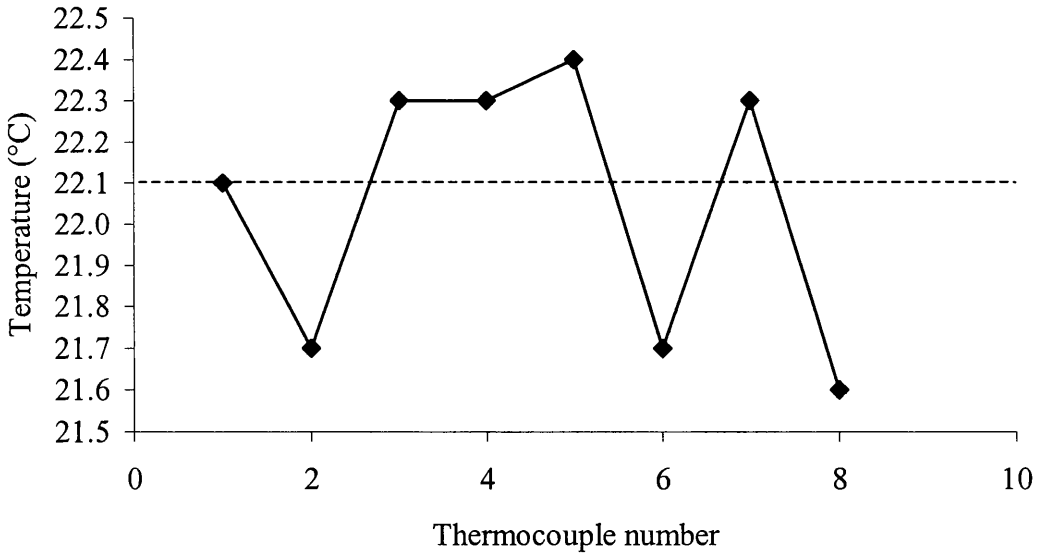


Figure 3.2: Graph showing the readings of the thermocouples at room temperature. The dashed line shows the room temperature.

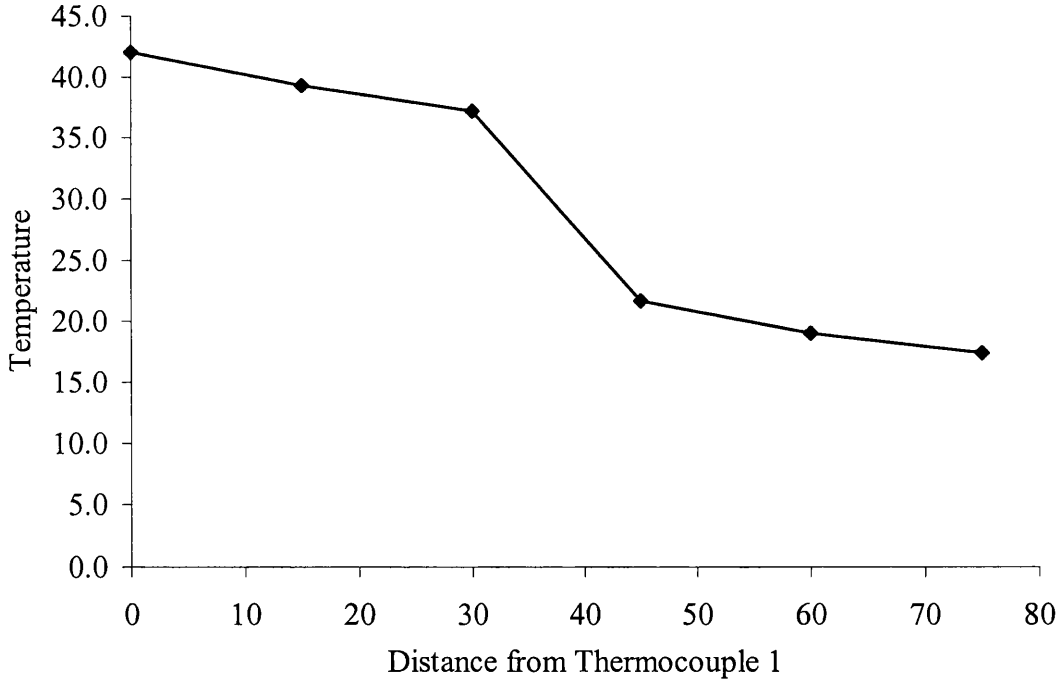


Figure 3.3: Example of a temperature curve.

From such a plot, the temperature difference across the sample can be easily deduced.

There are two important factors that need to be considered to allow good calibration of the thermal conductivity equipment. The first is that some heat may be lost sideways through the thermal insulation and so not pass through the sample. The second is that the interface between the brass cylinders and the sample may not be a good thermal interface. Thermally conductive grease was used to improve this situation, but it will certainly present a thermal barrier to some degree.

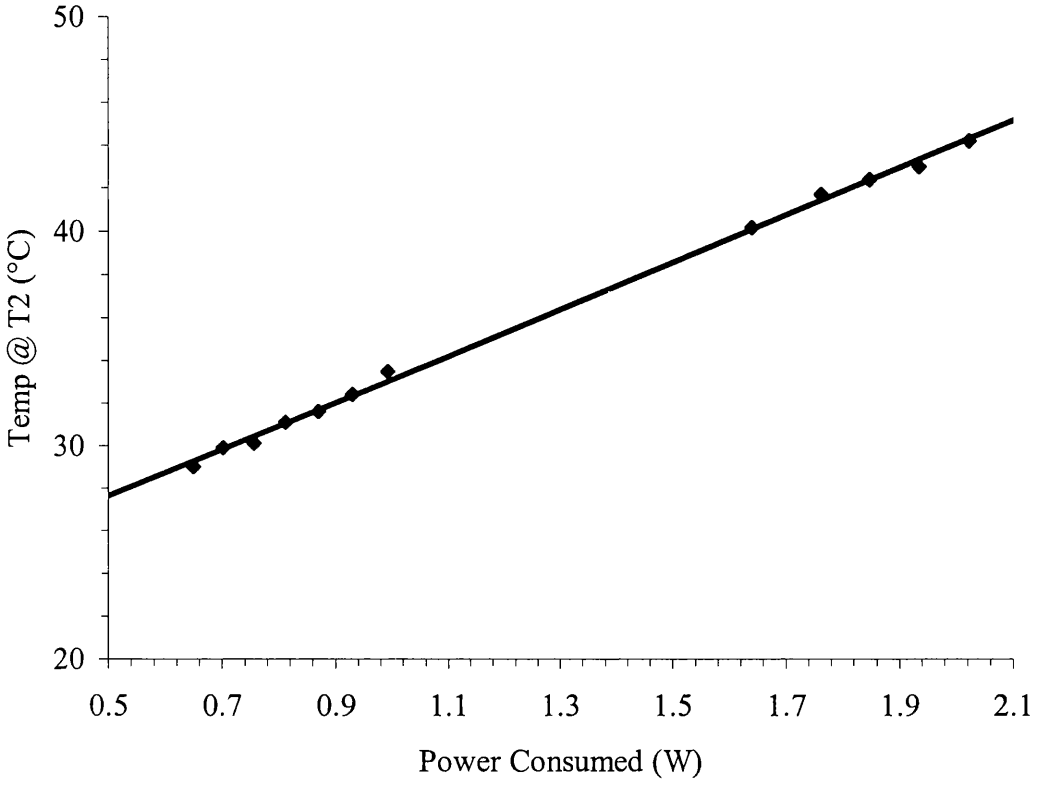


Figure 3.4 Calibration plot for heat loss via the side-walls.

To assess the amount of heat lost via conduction through the thermally insulated sides, a series of tests was conducted with a thermally insulated air gap in place of the sample. The assumption with this was that negligible heat would be conducted across the air gap and so all the heat input would be dissipated through the sidewalls. Tests were run at a range of heater voltages (hence heat inputs), and the thermocouple temperatures recorded for each heat input. The results of this calibration are shown in Figure 3.4. This shows that as the temperature at T2 increases, the amount of heat lost also increases in a linear fashion. From this graph, it is possible to calibrate each thermal conductivity

measurement, by determining the heat lost at a particular operating temperature (which was normally about 30 - 32 C), and then subtracting this from the measured value of Q. This procedure was performed for all tests.

The second calibration concerned the heat lost at each interface. To determine this, a calibration block of brass (containing two thermocouples) was used in place of the sample, with the thermally conductive paste at each interface. From these tests, it was found that at a heat flow of 5.04 W, there was an average temperature drop at each interface of 0.34 C. This is demonstrated in Figure 3.5.

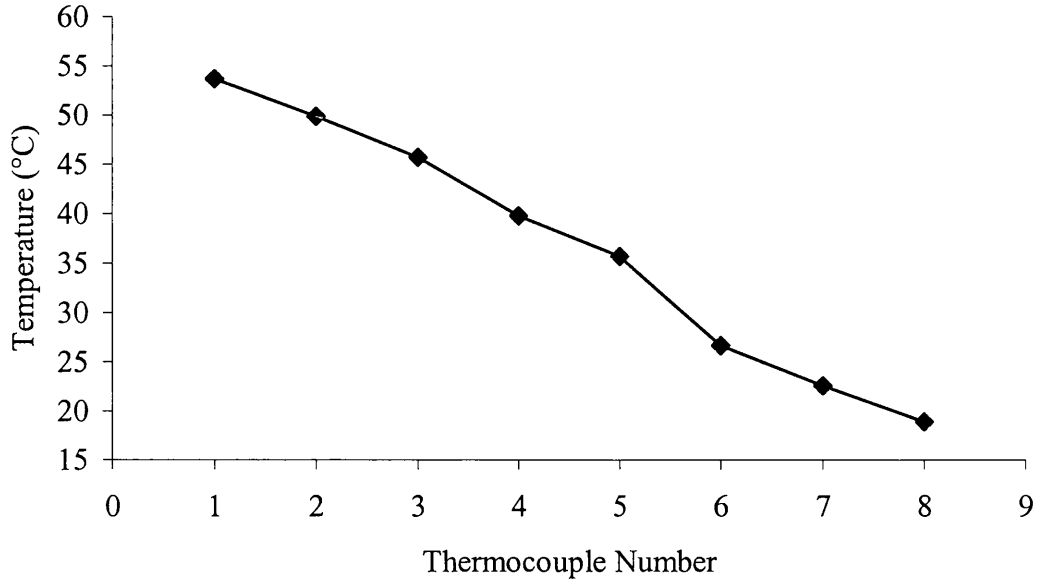


Figure 3.5: Example of readings from a calibration of the thermal barrier between surfaces.

If it can be assumed that the thermal conductivity of the paste, and the paste layer thickness are constant, then from the Fourier equation, we can deduce that:

$$\frac{x}{k} = \frac{\Delta TA}{Q} = 33.1x10^{-6}$$

Using this, it is possible to determine the temperature drop at each interface, for any value of area A and heat flow Q :

$$\Delta T = 33.1x10^{-6}\frac{Q}{A}$$

This calibration was also used for all tests.

The final method for determining thermal conductivity was as follows:

- Samples of approximate dimensions 10 mm x 10 mm x 2 mm were placed in the test equipment.
- Thermally conductive paste was applied at each interface.
- A weight (10 N) was placed on top of the equipment to ensure good contact to the sample.
- The cooling water was set at a constant flow rate.
- The heater was set at 5 W and allowed to equilibrate (normally for at least 3 hours).
- The temperature of each thermocouple was recorded when values had settled.
- The calibrations described above were performed.
- The graph of temperature versus height was plotted.
- The temperature drop across the sample was determined, from which the thermal conductivity could be calculated.

3.2 Scanning Electron Microscopy

To observe the microstructure of the samples, the best method was found to be scanning electron microscopy of a cut section through the sample. This showed the particle distribution, degree of bonding between polymer and particles and the levels of porosity very well. Prior to examination, all samples were given a light coating of gold to avoid charging effects.

3.3 Mechanical Testing

To determine the effect of filling on the tensile strength and stiffness of the materials, tensile tests were performed on some of the samples. The number of these tests were limited due to the size of sample needed. For the tests that were conducted, strips of material, of approximate dimensions 20 mm x 6 mm x 2 mm were used. These were tested in an Instron electromechanical testing machine at a test speed of 10 mm / min. Tests were conducted to failure, with a continuous recording of force against extension, from which graphs of stress against strain were produced.

3.4 Dynamic Mechanical Thermal Analysis

To determine the temperature dependence of stiffness, dynamic mechanical thermal analysis (DMTA) tests were conducted on a limited number of samples over a temperature range from -70 to +100 C. These tests were conducted on thin strip samples, clamped in tension and continuously deformed dynamically (amplitude 20 μm) at a frequency of 1 Hz. The temperature was increased from -70 to +100 at a rate of 2 degrees per minute. A continuous record of tensile modulus and damping (tan δ) was recorded. Again, these tests were limited due to the size of specimens needed.

3.5 Thermal Expansion

The thermal expansion was also measured for some samples using the DMTA equipment. In this case, strip samples were held at zero force as the temperature increased from 30 C to 100 C. This produced a record of the sample length versus temperature, which varied quite linearly. The thermal expansion coefficient was determined from the slope of this variation, divided by the original length.

3.6 Structural Constituent Materials

Diamond is in many ways an excessive material, it has values of mechanical hardness, strength and compressibility that exceed all comparable values for other substances. An example of a few of the characteristics of the material are shown in table 3.1 (43).

Table 3.1 Some of the properties of diamond.

Mechanical Hardness (~90GPa).
Strongest known material, highest bulk modulus (1.2 x 10^{12} N/m^2), lowest compressibility (8.3 x 10^{-13} m^2/N).
Highest known value of thermal conductivity at room temperature (2 x 10^3 W/m/K).
Thermal expansion coefficient at room temperature (0.8 x 10^{-6} K)
Broad optical transparency from the deep UV to the far IR region of the electromagnetic spectrum.
Good electrical insulator (room temperature resistivity is ~10^{16} Ω cm).
Diamond can be doped to change its resistivity over the range 10-10^{16} Ωcm so becoming a semi-conductor with a wide band gap of 5.4 eV.
Very resistant to chemical corrosion.

3.6.1 Chemical Vapour Deposition Synthesis Of Diamond

Chemical vapour deposition involves a gas phase chemical reaction occurring above a solid surface, which causes deposition onto that surface. All CVD techniques for producing diamond films require a means of activating gas-phase carbon-containing precursor molecules. This generally involves thermal (*e.g.* hot filament) or plasma (D.C., R.F., or microwave) activation, or use of a combustion flame (oxyacetylene or plasma torches). Figure 3.6 illustrates two of the more popular methods and gives some typical operating conditions. Whilst each method differs in detail, they all share features in

common. For example, growth of diamond (rather than deposition of other, less well-defined, forms of carbon) normally requires that the substrate be maintained at a temperature in the range 1000-1400 K, and that the precursor gas be diluted in an excess of hydrogen (typical CH_4 mixing ratio ~1-2vol%).

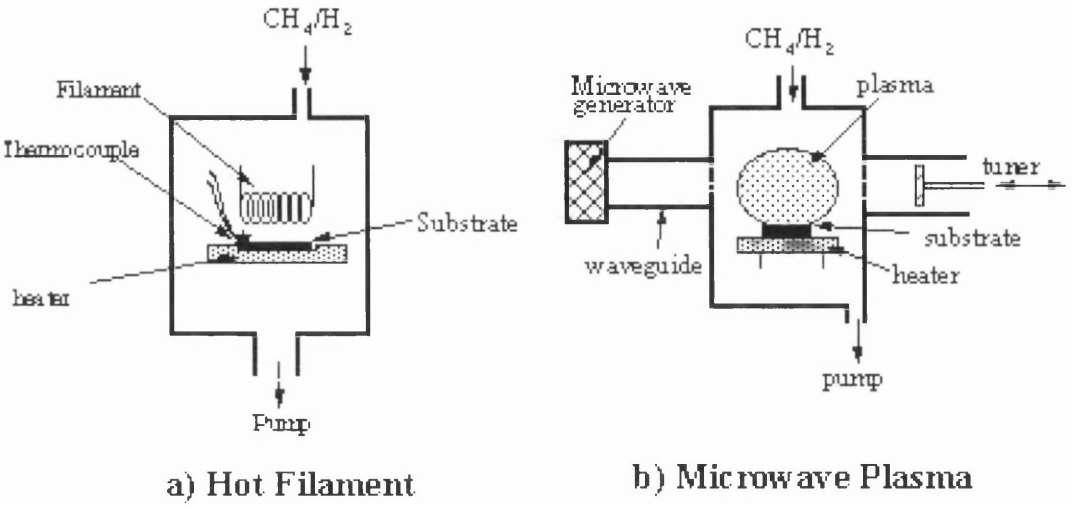


Figure 3.6 Examples of two of the most common types of low pressure CVD reactor. (a) Hot filament reactor, (b) Microwave plasma enhanced reactor.

The resulting films are polycrystalline, with a morphology that is sensitive to the precise growth conditions. Growth rates for the various deposition processes vary considerably, and it is usually found that higher growth rates can be achieved only at the expense of a corresponding loss of film quality. 'Quality' here is a subjective concept. It is taken to imply some measure of factors such as the ratio of sp3 (diamond) to sp2-bonded (graphite) carbon in the sample, the composition (*e.g.* C-C versus C-H bond content) and the crystallinity. In general, combustion methods deposit diamond at high rates (typically 100-1000 μm/hr, respectively), but often only over very small, localised areas and with poor process control leading to poor quality films. In contrast, the hot filament and plasma methods have much slower growth rates (0.1-10 μm/hr), but produce high quality films. One of the great challenges facing researchers in CVD diamond technology is to increase the growth rates to economically viable rates, (hundreds of μm/h), or even mm/hr) without compromising film quality. Progress is being made using microwave deposition reactors, since the deposition rate has been found to scale approximately linearly with applied microwave power. Currently, the typical power rating for a microwave reactor is

~5 kW, but the next generation of such reactors have power ratings up to 50-80 kW. This gives a much more realistic deposition rate for the diamond, but for a much greater cost.

Thermodynamically, graphite, not diamond, is the stable form of solid carbon at ambient pressures and temperatures. The fact that diamond films can be formed by CVD techniques is inextricably linked to the presence of hydrogen atoms, which are generated as a result of the gas being 'activated', either thermally or via electron bombardment. These hydrogen atoms are believed to play a number of crucial roles in the CVD process:

- They undergo H abstraction reactions with stable gas-phase hydrocarbon molecules, producing highly reactive carbon-containing radical species. This is important, since stable hydrocarbon molecules do not react to cause diamond growth. The reactive radicals, especially methyl, CH_3, can diffuse to the substrate surface and react, forming the C-C bond necessary to propagate the diamond lattice.
- H-atoms terminate the 'dangling' carbon bonds on the growing diamond surface and prevent them from cross-linking, thereby reconstructing to a graphite-like surface.
- Atomic hydrogen etches both diamond and graphite but, under typical CVD conditions, the rate of diamond growth exceeds its etch rate whilst for other forms of carbon (graphite, for example) the converse is true. This is believed to be the basis for the preferential deposition of diamond rather than graphite.

For the majority of samples a natural diamond powder with a size range between 8 and 16 μm was used. A limited number of samples were also produced with synthetic particles of various size ranges from 1 to 45 μm.

CHAPTER 4 DIAMOND-FILLED SILICONE ELASTOMERS

The silicone elastomer used for the bulk of the work was a flowable one-part curable RTV elastomer which was purchased from GE Silicones (Grade TSE399-C). The main reason for choosing this material was for its low viscosity before curing. This was needed to allow sufficient mixing of the high diamond loadings. Full details of this material are given below (from GE Silicones data sheet).

4.1 Data On TSE399 Silicone Elastomer

TSE392, TSE397 and TSE399 adhesive/sealants/coatings are one component RTV's that cure quickly by reacting with atmospheric moisture forming a soft dielectric silicone rubber. These materials incorporate a newly developed crosslinking chemistry and are non-corrosive to metallic substrates. They are particularly well suited for electrical/electronic applications.

This series of products differ in consistency, TSE392 is a thixotropic paste, TSE397 is semi-flowable, and TSE399 is flowable. When cured, they retain their elastomeric properties throughout the operating range of temperature from -55C to 200°C (-67F to 392F).

PRODUCT FEATURES

- Meets the corrosion resistant requirements of MIL-A-46146A*
- Fast cure at ambient temperatures
- Odour, slight alcohol
- Outstanding adhesion, including most plastics
- Outstanding electrical properties
- Resistant to heat, cold, moisture, UV, ozone and chemicals

PRODUCT BENEFITS

- One component, no mixing or de-airing required
- Soft consistency provides protection against mechanical and thermal shock

- Excellent electrical insulation
- Protects against moisture
- Varying viscosities allow thorough coating around complex assemblies (TSE399) and thicker coatings where required i.e., high voltage components (TSE392 & TSE397).
- Convenient packaging/dispensing tubes or cartridges.

* Does not meet hydrolytic stability requirement of MIL-A-46146A

Uncured Properties	**TSE392**	**TSE397**	**TSE399**
Cure System	Alkoxy	Alkoxy	Alkoxy
Colours Available	Clear /White	Clear/White	Clear/White/Black
Consistency	Thixotropic Paste		Semi Flowable Flowable
Viscosity, cps (@ 25°C)	-	50,000	2,500
Tack Free Time, mins	5	10	10
Cured Properties			
Specific Gravity	1.04	1.04	1.04
Hardness (JIS A)	30	20	30
Tensile Strength, kgf/cm^2	16	12	13
Elongation, %	400	300	140
Useful Temperature Range (Continuous) °C	-55 to 200	-55 to 200	-55 to 200
Dielectric Strength , kV/mm	22 (560)	22 (560)	20 (510)
Dielectric Constant (60 Hz)	2.9	2.9	2.9
Dissipation Factor (60 Hz)	0.005	0.005	0.005
Volume Resistivity,	$2x10^{15}$	$2x10^{15}$	$2x10^{15}$

Surface Preparation

To prepare a good bond, it is necessary to ensure that surfaces to be sealed, coated or bonded are clean and free of grease, lubricating oils, release agents and dirt. To optimise fast cure and good adhesion, substrates must be thoroughly dry of cleaning solvents before applying the RTV. The RTV should be applied to one surface only. Excess uncured material should be wiped away with a clean cloth. After curing, removal of material is more difficult.

Bonding

These products offer primerless adhesion to many substrates including most plastics. Maximum adhesion is obtained 72 hours after full cure is obtained (2 mm thick specimen to an aluminium substrate).

Curing

These products cure at room temperature reacting with atmospheric moisture. Whenever possible, 25°C and 50% relative humidity should be provided. Higher temperature and humidity will cause faster cures while lower temperatures and lower humidity will slow the cure considerably.

These products cure from the outside (outer skin) inward, therefore, cure rate is also dependent on the thickness of the material. It is not recommended to apply material thicker than 6 mm.

In addition to the above, some samples were produced using a two-part RTV material from Ambersil.

4.2 Sample Production

A considerable amount of the effort involved in this project has been focussed on optimising the sample production method. This has been a gradual process as the following factors have had to be considered:

- Mixing method
- Mixing time
- Curing time
- Sample shape
- Curing under ambient conditions, pressure or vacuum
- Post-curing

The key problems to be overcome have included the following:

- Steep increase in viscosity as high diamond loadings are mixed.
- Introduction of porosity during the mixing process.
- Ensuring sufficient moisture ingress to produce curing.

The development of sample production is outlined below. For some of these stages, photographs of typical samples have been included.

4.2.1 Initial method

This involved weighing a certain amount of diamond powder, adding the required weight of silicone (generally about 20-30%), followed by a period of about 5 minutes of intense hand mixing. The material was then compacted into a simple mould consisting of a small of a silicone tube. This produced small cylindrical samples, which were initially considered to be ideal for thermal conductivity measurements. These cylinders typically took about two days to fully cure.

It was found that the samples had considerable levels of porosity from the mixing process (seen in Figure 4.1). It was also found that the thickness of the samples produced in this

way (about 15 mm) was too great for accurate thermal conductivity measurements. It was thought that the thickness of the sample could lead to the centre not curing. This, however, was not a problem.

It was clear that samples needed to be thinner and that some method of reducing porosity levels was needed.

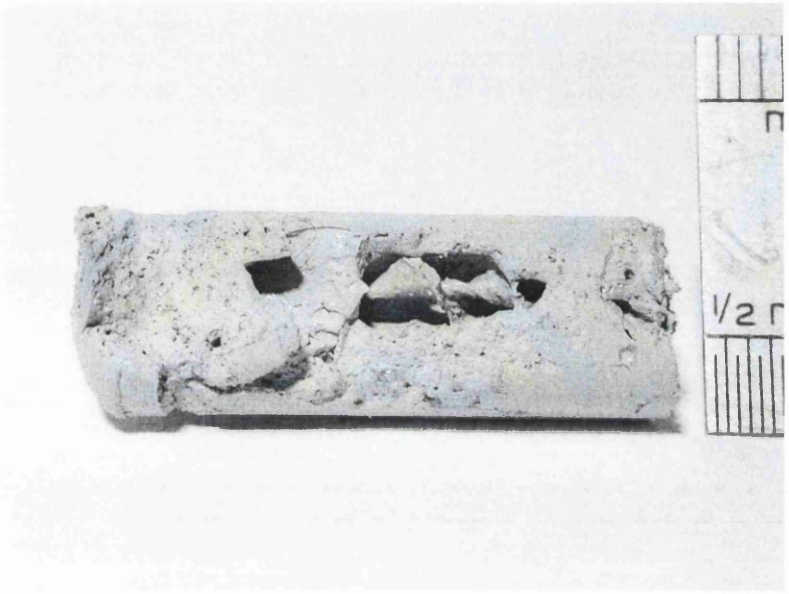


Figure 4.1 A cross section of an initial tubular sample.

4.2.2 Slightly compressed disks

The second method involved pressing the mixed silicone into the form of a thin disk (about 2 mm thick), between two sheets of polyethylene. A small weight (10N) was then placed on top to give some compression. This method was reasonably successful, with good rates of curing (within one day), but porosity was still a problem, as seen in Figure 4.2.

Figure 4.2 An initial disk sample

4.2.3 Disks with solvent additions

As a method of reducing the viscosity during mixing a small amount of a volatile, but unreactive solvent (petroleum ether) was added. This did allow greater mixing at the high filler loading levels, but also led to extra porosity as the solvent evaporated. A balance was therefore struck, adding just sufficient solvent to allow a good mix.

4.2.4 Vacuum bag method

As an attempt to reduce levels of porosity, a vacuum bagging system was developed. This involved placing the mixed material, roughly compressed into a disc, into a small polyethylene bag, which was then attached to a vacuum pump. This enabled any excess entrapped air and volatiles produced during curing to be removed. This method did produce a lower level of porosity generally, but a few large central pores were still evident. It also resulted in slightly longer curing times (up to two days) and as no external compression was used, the sample surfaces were more uneven (Figure 4.3).

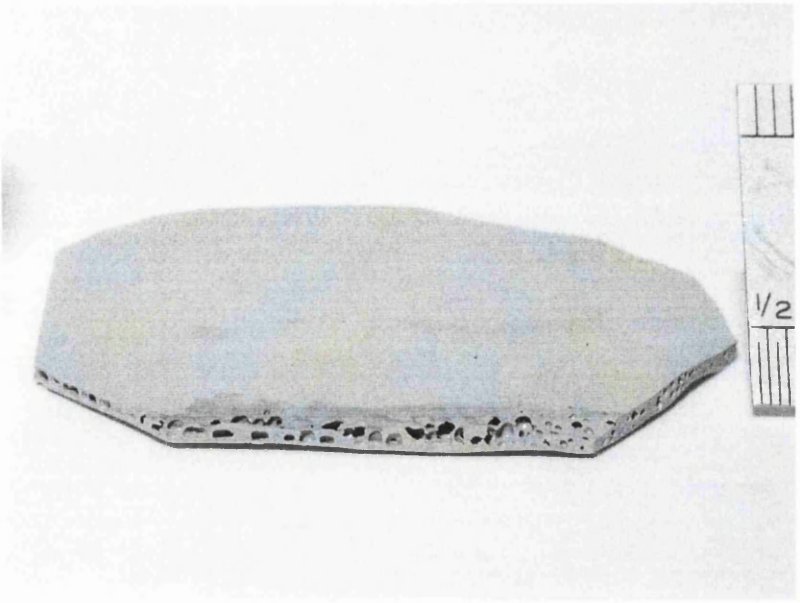


Figure 4.3 A vacuum bagged sample

4.2.5 Compression moulding

The most successful method was that using compression moulding equipment. In this case, the mixed material was pressed into a disc-shaped mould, polyethylene sheets were placed above and below the disk and then the sample was compressed in a compression moulder, at a pressure of about 2 MPa. Although this produced samples with lower levels of porosity, and with reasonably flat surfaces, the curing rates were reduced quite dramatically. With many of the samples, curing took about 4 - 5 days to complete. The main reason for this is likely to be the fact that there was very little access for atmospheric moisture, which is needed to produce the curing. The situation was improved somewhat by cutting a small channel opening into the side of the mould, and by increasing atmospheric humidity levels during mixing. Despite these improvements, it remained a slow production route, but it was used for the majority of the best samples produced in the later stages of work. It was still subject to some variability in terms of the degree of porosity, as seen with a comparison of Figures 4.4 and 4.5. To ensure good thermal contact for measurements of thermal conductivity, the faces of the samples were normally given a light abrasive treatment to obtain as flat a surface as possible.

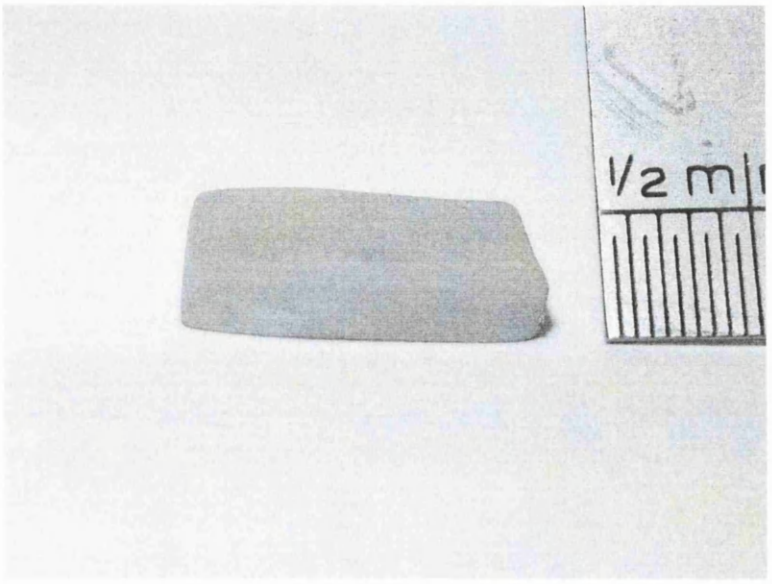


Figure 4.4 A good sample produced by the compression moulding method

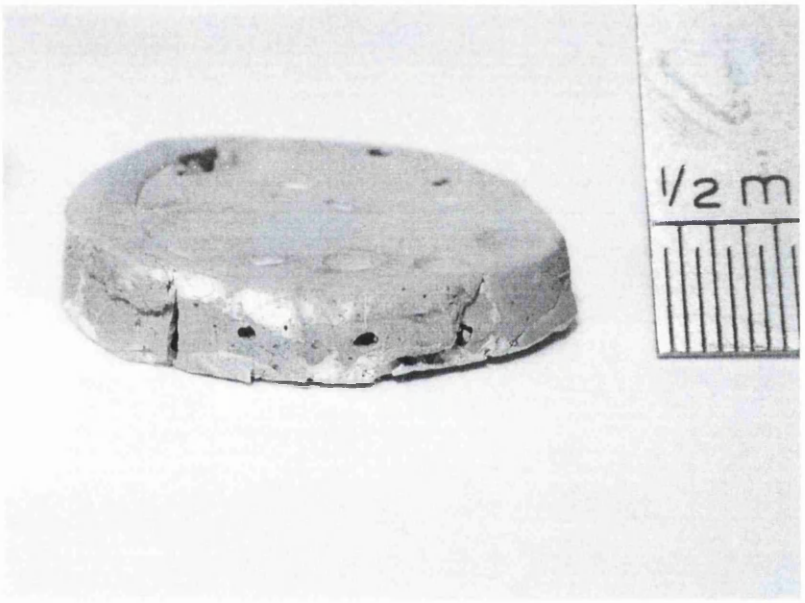


Figure 4.5 A poor sample produced by the compression moulding method.

4.2.6 Vacuum chamber method

One final method of reducing porosity was attempted, which was to mix and cure the sample within a vacuum chamber. This produced the dramatic and undesirable effect of excessive porosity (almost foaming) as the entrapped air and volatiles were removed (Figure 4.6). This excessive foaming meant that it was impossible to produce a sample sufficiently coherent to measure the thermal conductivity. It is clear that the ideal method would require some compression (to remove any pores in the structure) and some vacuum

(to remove gases). It is practically difficult to apply both of these methods at once. It has been found that compression alone is better than vacuum alone.

Figure 4.6 The 'foamed' sample produced using a vacuum chamber

4.2.7 Two-part silicone

A few samples were prepared using a two-part RTV silicone elastomer. In this case, the diamond powder was mixed with the prepolymer. Once a sufficient mix had been achieved, the catalyst was added in. This should have given the advantage that the mixing process could be completed before any curing occurred. Although a reasonable mix was achieved, curing did not occur, even after several days and a post-curing heat-treatment. The reasons for this lack of curing are not clear (an unfilled sample cured without problems). It is likely that the adsorbed water on the diamond particles is inhibiting the curing reaction, possibly by shielding the alcohol groups on the prepolymer from the crosslinking agent.

4.3 Results

The following results highlight the important values obtained for samples throughout the development. Alongside the conductivity results, details of the sample production behaviour and microstructures are also given.

4.3.1 Initial Results

Unfilled silicone was tested and found to have a thermal conductivity of 0.24 W/mK. As no viable specimens were produced using the initial method of production it was not possible to test the conductivity of these.

Next, disks that were produced by the method of being slightly compressed as described in section 4.2.2 were tested. Samples of concentrations of 75% and 82% by weight were tested. The sample of concentration 75% wt (47% diamond by volume) had a thermal conductivity of 0.55 W/mK. The samples produced and tested had a significant degree of porosity as seen in Figure 4.7. Samples filled to 82% wt were then tested and found to have large degrees of porosity. These early samples of 82% wt filled had a thermal conductivity of 0.76 W/mK and are shown in Figure 4.8. After repeated attempts and refinements of the slightly compressed method of production a sample was produced with very little porosity, this is shown in Figure 4.9. This improved sample was found to have a thermal conductivity of 2.15 W/mK showing the dramatic effect that a reduction in porosity can have.

A comparison of the samples consisting of 82% wt diamond at a higher magnification is shown in Figures 4.10 and 4.11. These show how the bonding of particles differs between a sample of good mixing and low porosity and one where the dispersion of the matrix material is uneven and large pores present. While throughout the production process the use of the structural constituent material has been kept to a minimum it is the thermal barrier presented by pores that cause the greatest reduction in thermal conductivity.

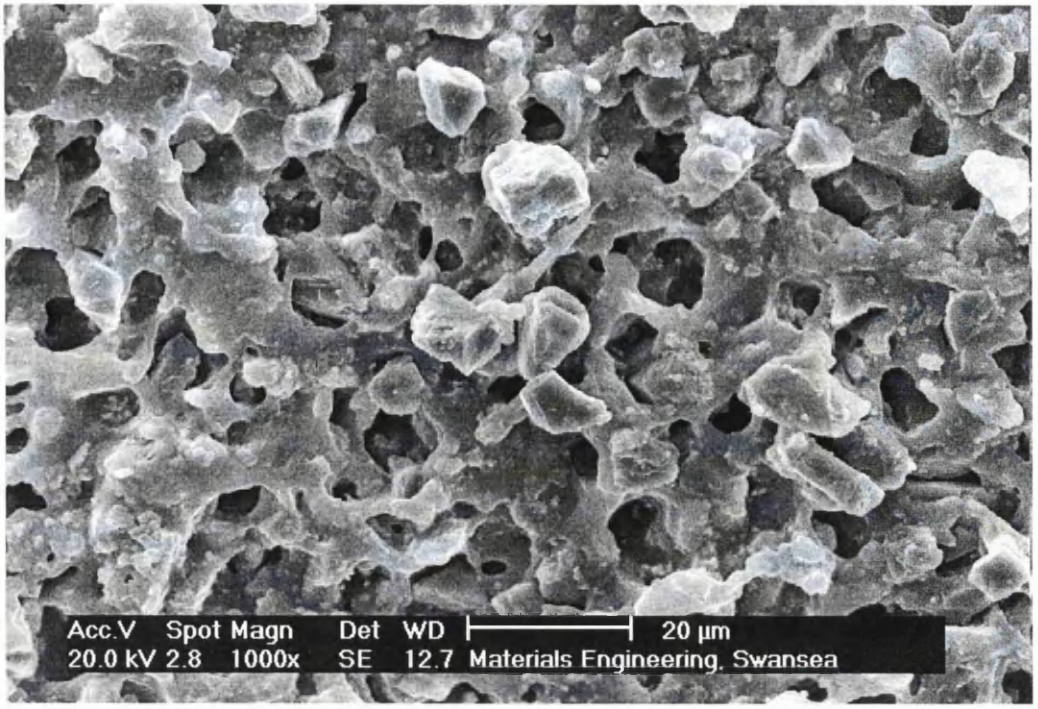


Figure 4.7 A sample of 75%(wt) produced as a lightly compressed disk showing high levels of porosity.

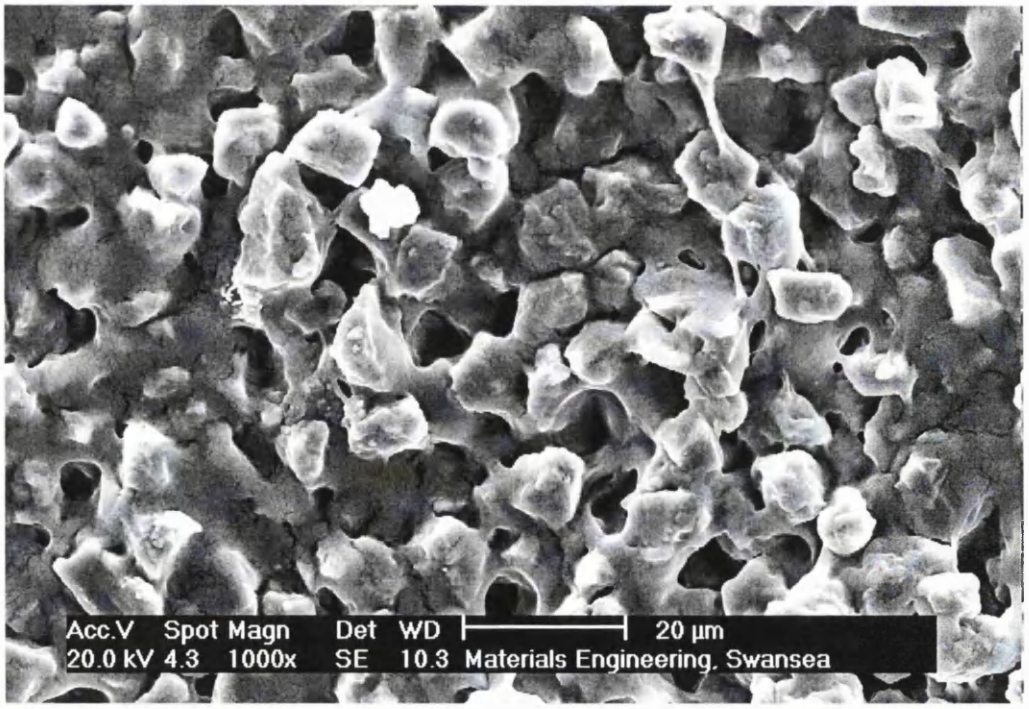


Figure 4.8 A sample of 82%(wt) produced as a lightly compressed disk showing high levels of porosity.

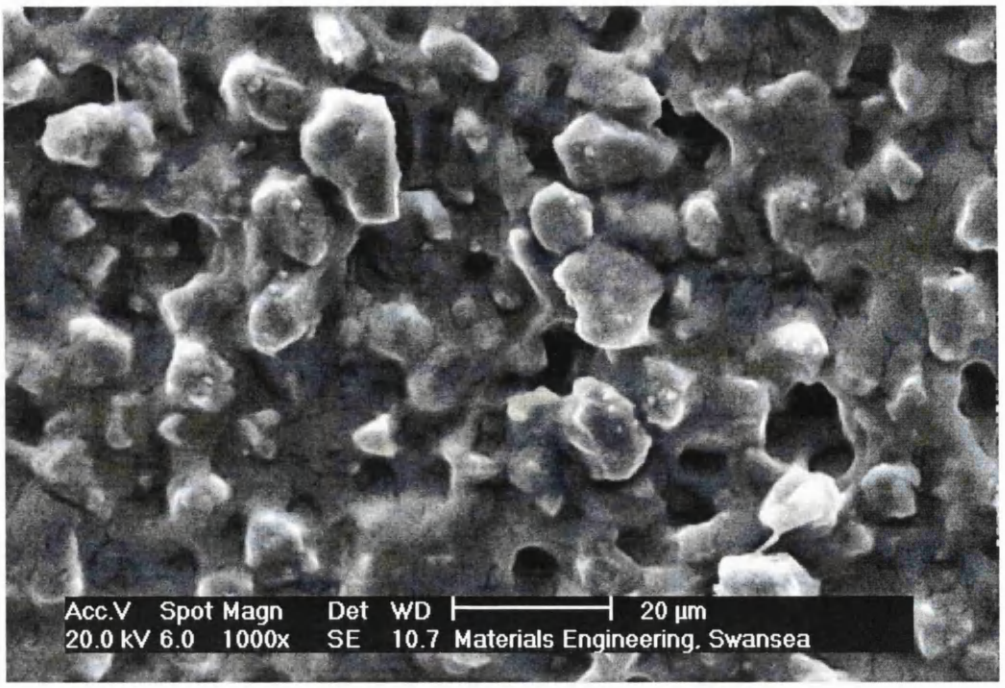


Figure 4.9 A sample of 82%(wt) produced as a lightly compressed disk showing low levels of porosity.

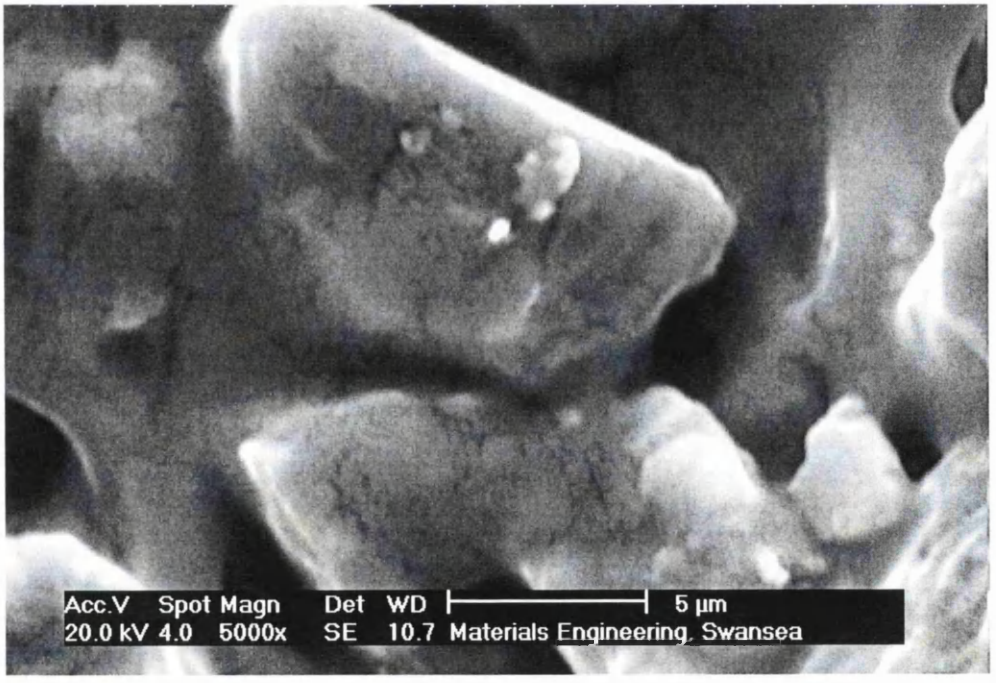


Figure 4.10 A magnified view of figure 4.9 showing excellent bonding between the diamond particles and the silicone matrix.

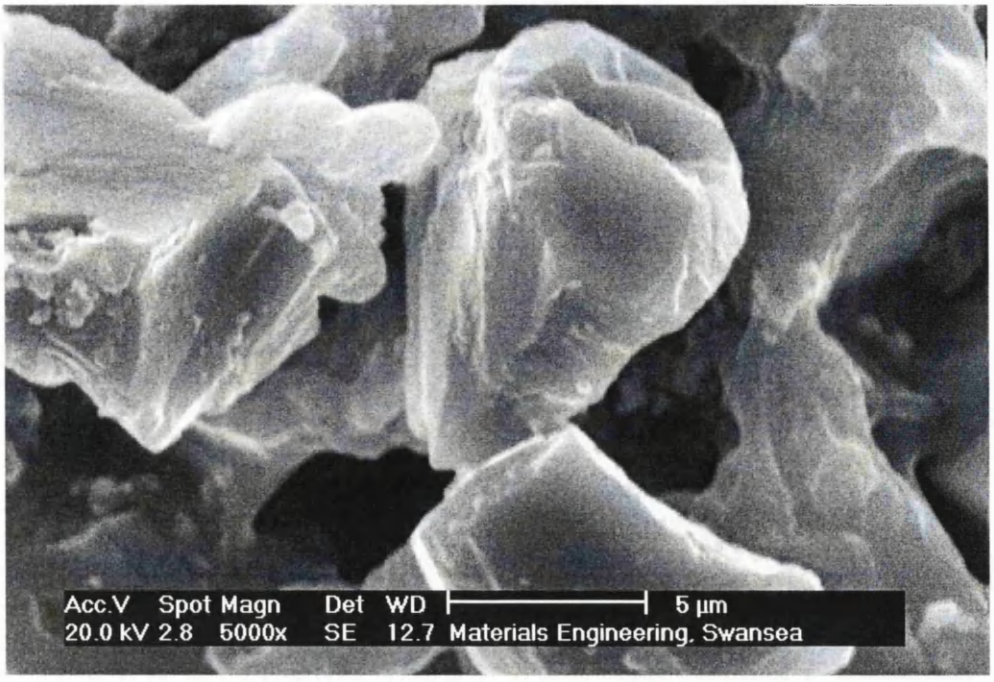


Figure 4.11 A higher magnification of the sample in figure 4.8. This shows poor bonding between the particles and matrix, it also shows a high degree of porosity in the sample.

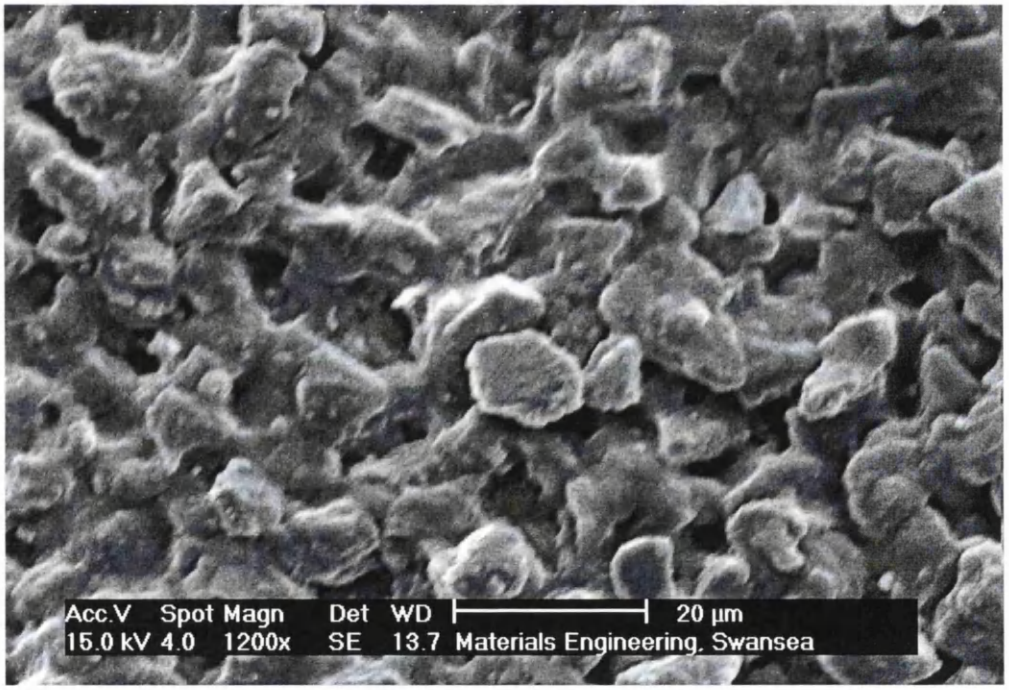


Figure 4.12 A sample produced using the vacuum bagged sample method.

As can be deduced from Figures 4.8-11 and the thermal conductivity measurements it was desirable to find a method of production that would allow the structural constituent to more evenly coat the diamond particles and allow the sample to be more fluid during production, thus reducing the amount of trapped pores as mixing is carried out. The addition of petroleum ether was there made as a solvent in the production process.

It was that thought that if the pores in the material were the greatest barrier to the increase of the thermal conductivity in the materials then a method of removing these would be the greatest step to making repeatable samples. In the above compression method it was thought that by applying a small pressure to the material would cause any voids to be minimised. To completely remove these voids it was decided that allowing the silicone to cure under a vacuum would be the ideal solution. This would force the voids to the surface during the period the sample was held under the low pressure. No problem was anticipated with the curing process as the diamond particles proved to be hydrophilic and were coated in a layer of water from the atmosphere. The thermal conductivity of the sample proved to be 0.30 W/mK and the porosity produced by this can be seen in Figure 4.12.

4.3.2 The Effects Of Diamond Content

A series of samples were produced at a range of diamond filler loadings, from 55% to 85% by weight using the natural diamond powder in the size range 8 - 16 μm. These are summarized in the table below:

55 wt%	27 vol%	Thermal conductivity of 0.64 W/mK (figure 4.13)
60 wt%	31 vol%	Thermal conductivity of 1.1 – 1.5 W/Mk
65 wt%	35 vol%	Thermal conductivity of 1.45 W/mK
70 wt%	41 vol%	Thermal conductivity of 1.34 W/mK (figure 4.14)
75 wt%	47 vol%	Thermal conductivity of 1.2 W/mK
80 wt%	54 vol%	Thermal conductivity of 2.34 W/mK (figure 4.15)
85 wt%	63 vol%	Impossible to make a coherent sample.

It is clear from these results that the diamond content has little effect between 60 wt% and 75 wt% and the variation between samples will be dictated by the levels of porosity. It can also be seen that as was earlier predicted there is a critical point below which (below 60 wt%) the thermal conductivity drops to approximately that of the matrix material and at the other end of the scale a upper critical point (above 75 wt%) at which the thermal conductivity of the material rapidly increases.

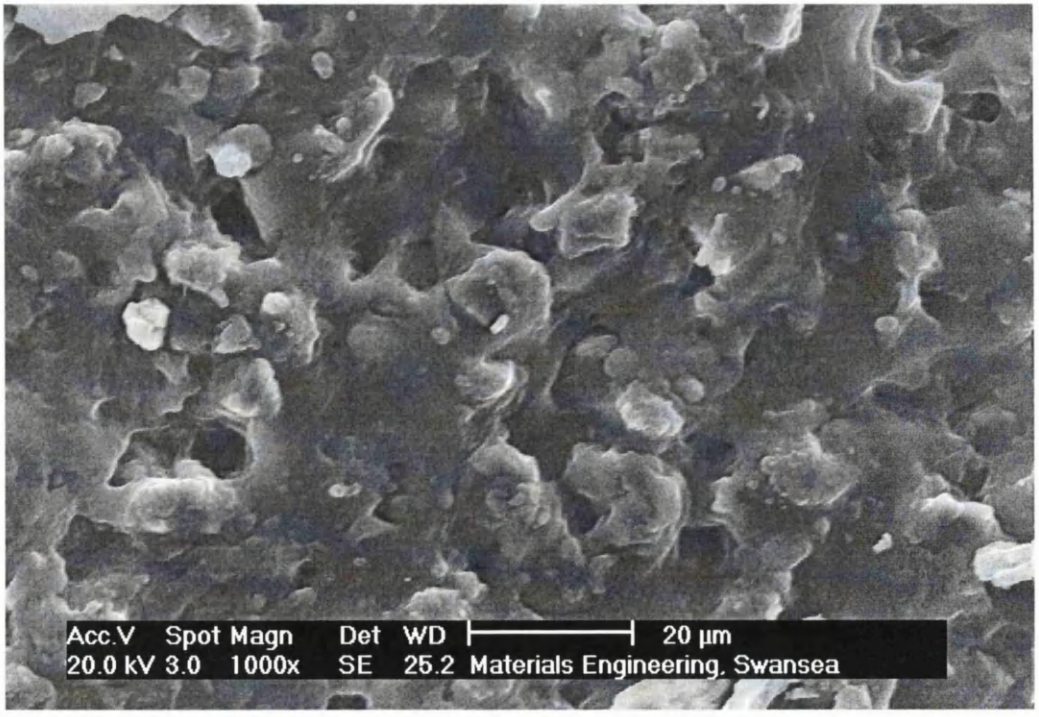


Figure 4.13 Silicone filled with 55 wt% (27vol%) natural diamond powder 8 - 16 µm.

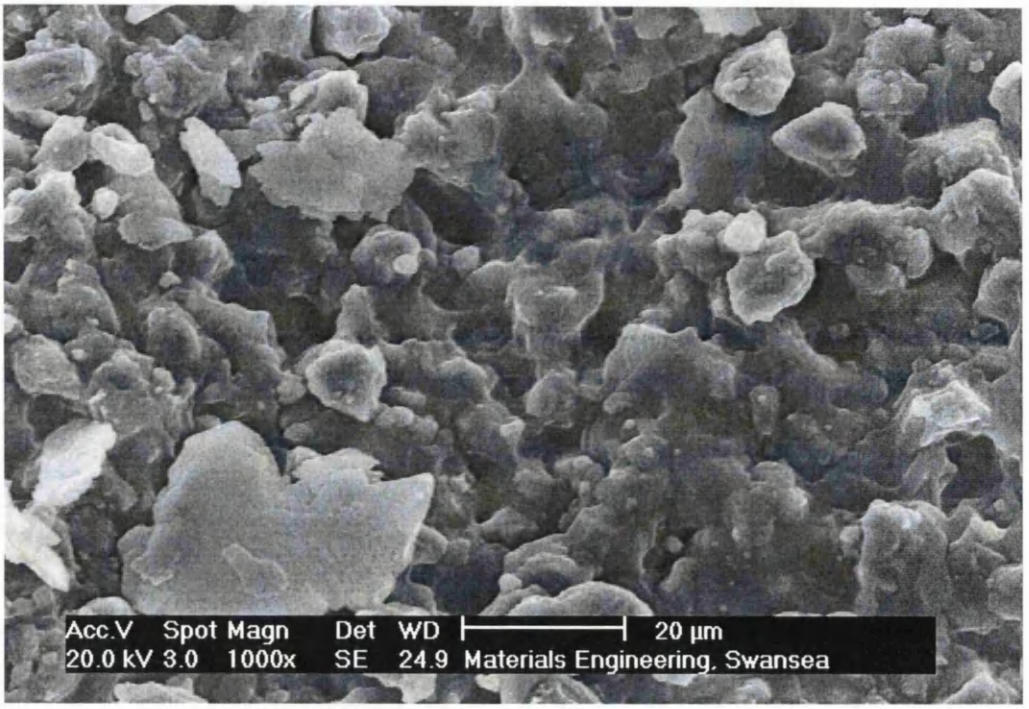


Figure 4.14 Silicone filled with 70 wt% (41vol%) natural diamond powder 8 - 16 µm.

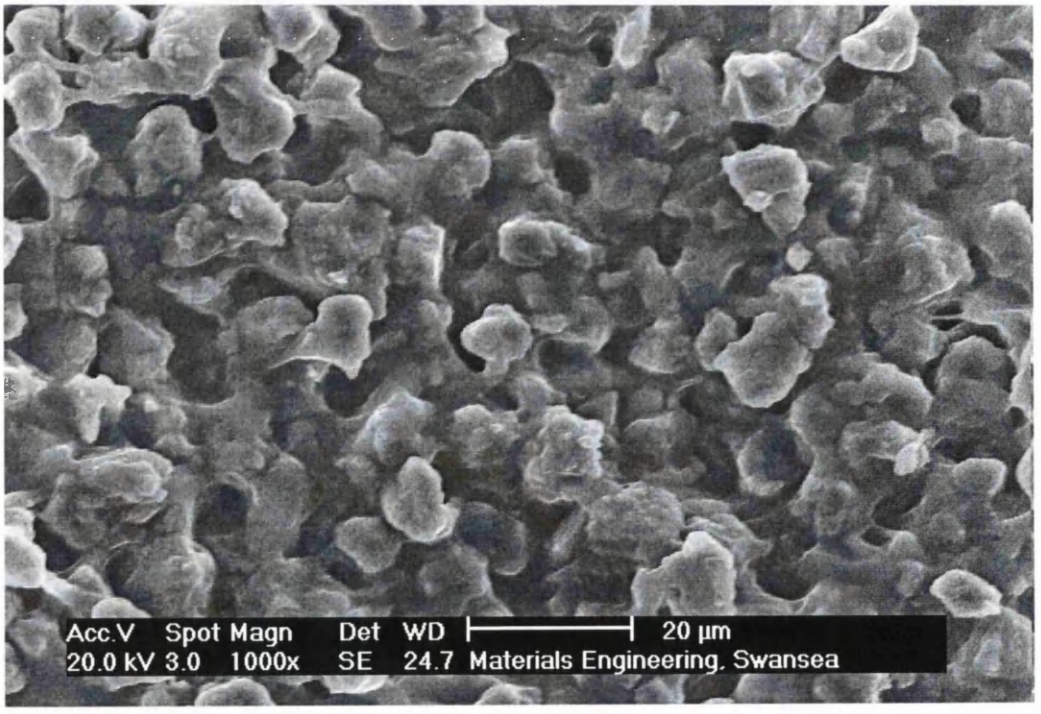


Figure 4.15 Silicone filled with 80 wt% (54vol%) natural diamond powder 8 - 16 µm.

4.3.3 The Effects Of Diamond Particle Size And Type

A number of samples were produced using other diamond particle types, to assess the effect of both particle size and type (synthetic versus natural). These were all made at approximately 80 % by weight diamond loading (54% by volume) if at all possible. The results are summarised below:

0-1 μm synthetic	Impossible to make coherent samples at 80% or 70% (fig 4.16)
4 μm synthetic	Impossible to make coherent samples at 80%
	70%: Thermal conductivity of 1.26 W/mK (fig 4.17)
15 μm synthetic	Thermal conductivity of 2.26 W/mK
45 μm synthetic	Thermal conductivity of 2.32 W/mK (fig 4.18)

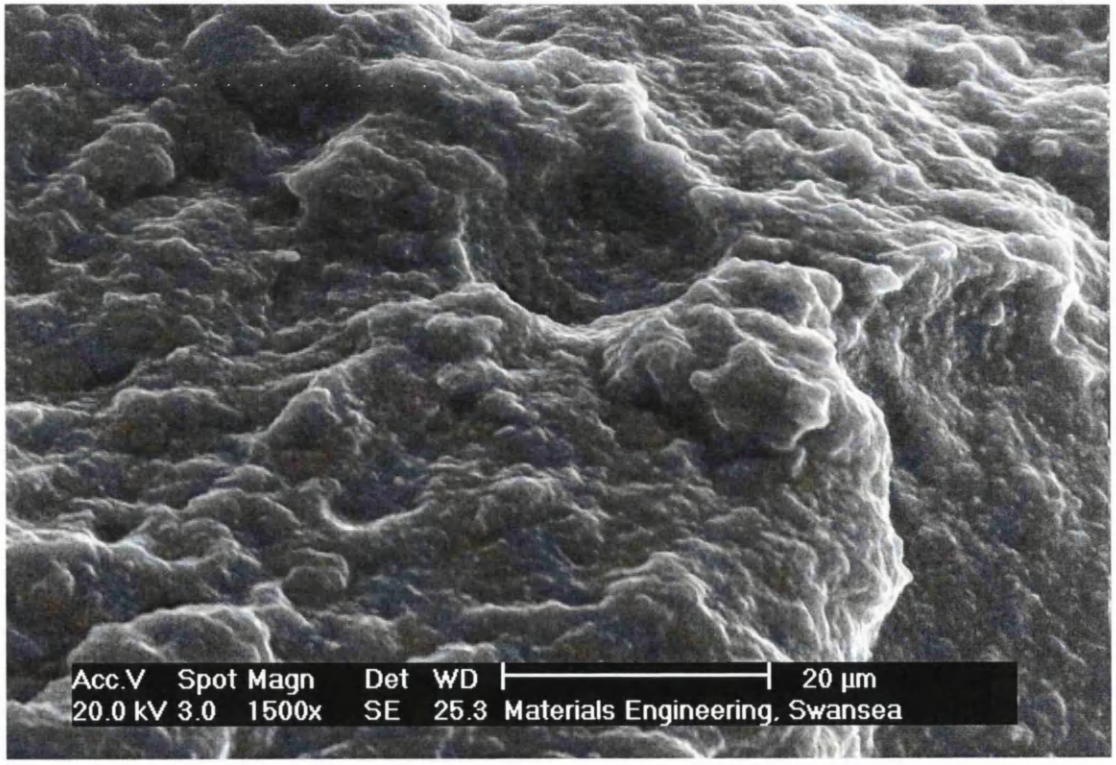


Figure 4.16 A sample containing 70wt% of 0-1 μm synthetic diamond powder

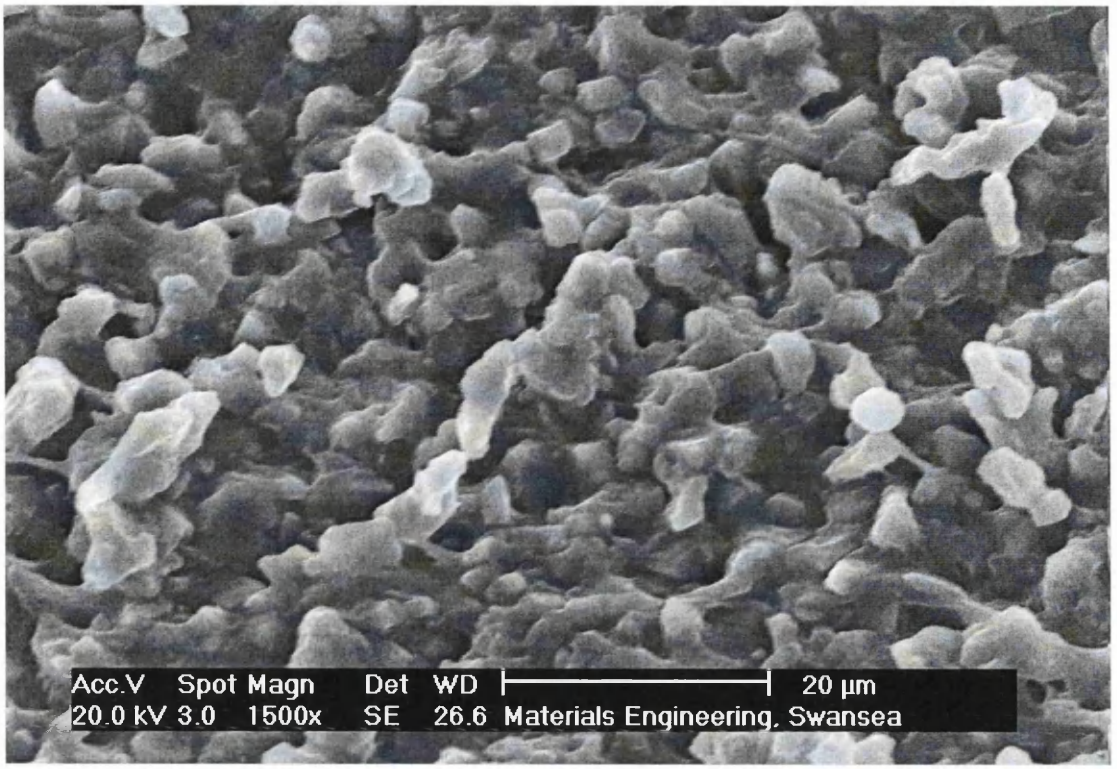


Figure 4.17 A sample containing 70wt% of 4 µm synthetic diamond powder

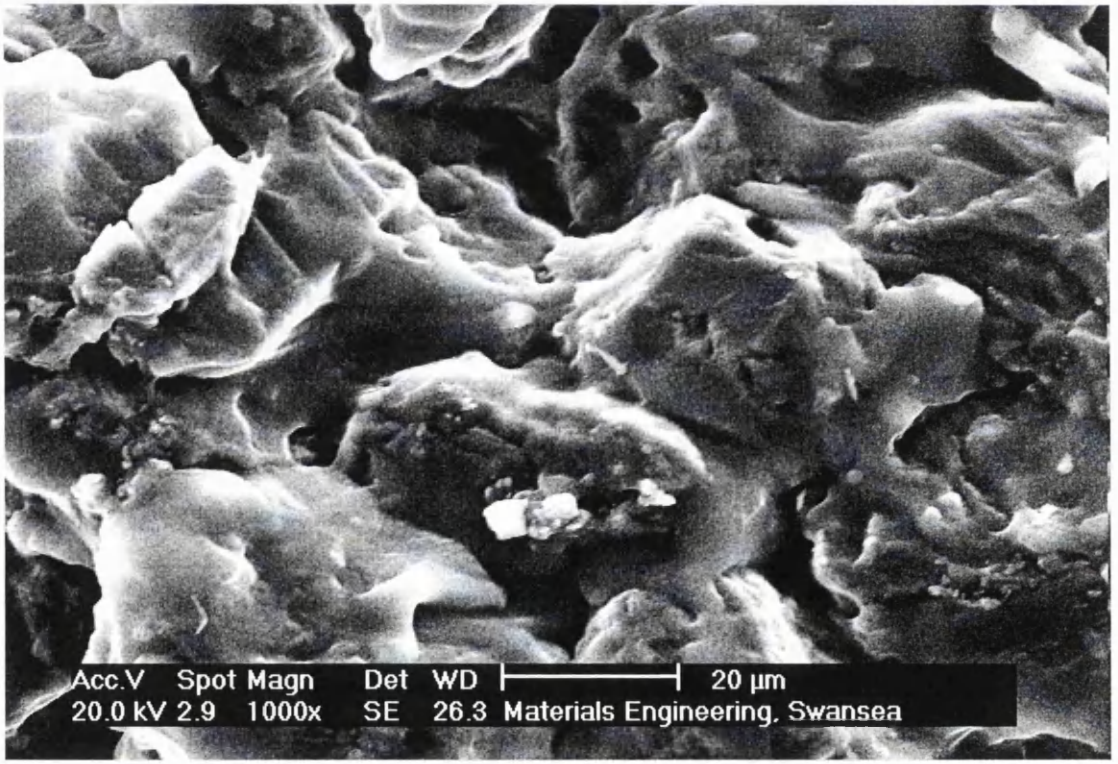


Figure 4.18 A sample containing 80wt% of 45 µm synthetic diamond powder

When comparing these results with those described above, it is clear that at a particular filler loading level, there is little effect of diamond particle size or type. The only important point is that with the smaller size particles, it becomes impossible to achieve high filler loadings.

4.3.4 Mixed Particle Sizes

The percolation theory of thermal conductivity via connecting particles states that there will be a critical point of filler level at which the there will be a dramatic jump in conductivity. These increases are not expected until the volume fraction rises well above 70% (weight fraction above 85%). If single sized particles are used, the maximum packing density that can be achieved is about 74% by volume, and so expected increases in thermal conductivity will only be moderate. It was thought that by using a mix of particle sizes, greater packing densities could be achieved and hence higher thermal conductivities. To this end, a sample of mixed particle size (mainly 45 μm, with about 20% of 15 μm and 10% of 4 μm) was produced.

With this mix, it was possible to make a sample with a total diamond loading of about 85%. This sample gave a thermal conductivity of 3.9 W/mK, significantly above any previous sample. The structure of this sample is shown in Figure 4.19 and 4.20, these figures clearly showing the reduction in the amount of porosity and the increase in packing density.

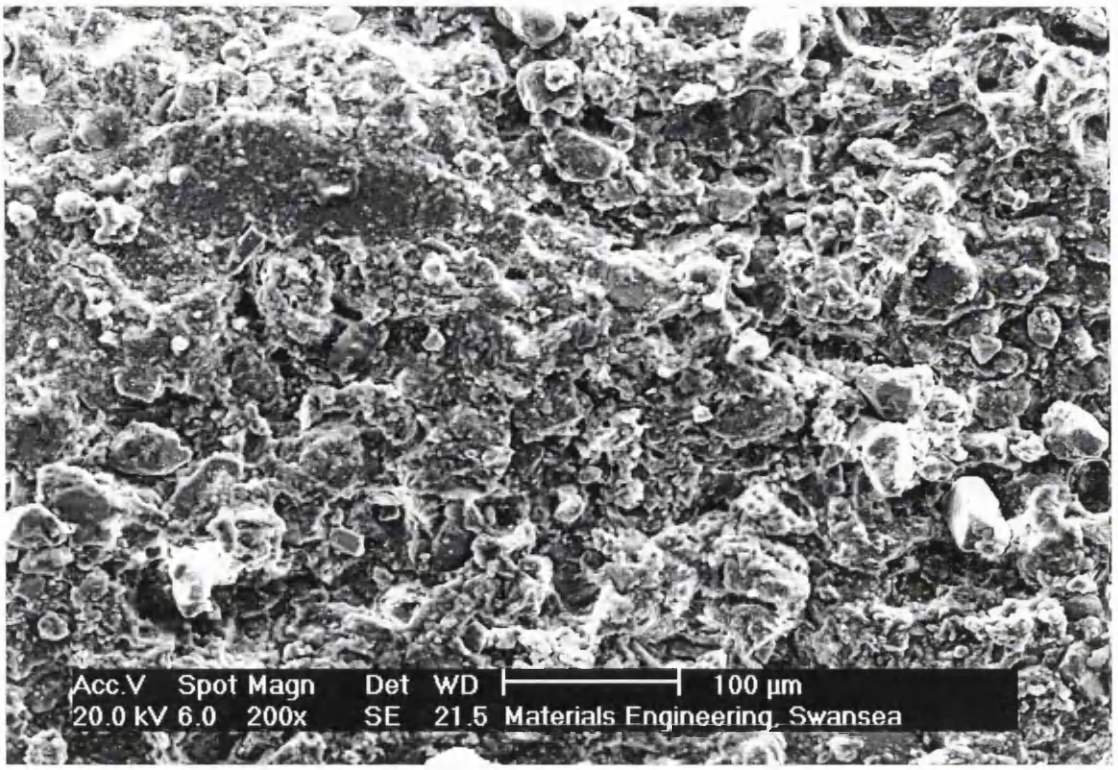


Figure 4.19 A sample containing mixed particle sizes at about 85% loading.

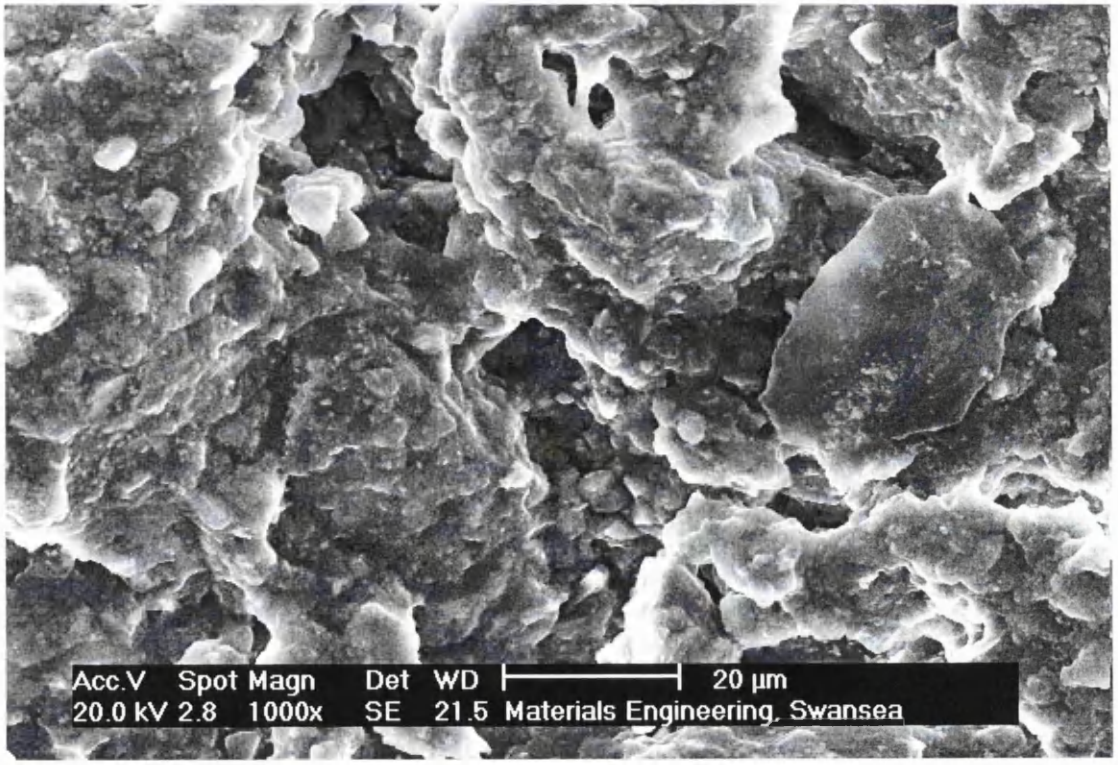


Figure 4.20 Higher magnification of Figure 4.19

4.3.5 Thermal Expansion Of Silicone Filled Polymers

The values of thermal expansion measured for certain samples are listed below. The samples were produced with the compression moulding technique, using the 8 - 16 μm natural diamond powder.

Unfilled Silicone	5.0×10^{-5} /°C
75% Filler loading	10.0×10^{-5} /°C
80% Filler loading	16.2×10^{-5} /°C

It is clear that as the diamond content increases, the coefficient of thermal expansion increases quite markedly, especially at the high filler loadings. This is quite surprising as diamond alone has an extremely low value of about 8×10^{-7} /°C. There is obviously some effect of the microstructure at play here, and may require further investigation.

4.3.6 Tensile Tests

The tensile tests performed on several samples are summarised in Figure 4.21. This shows the stress / strain behaviour for an unfilled silicone sample, and compression moulded samples containing 55%, 75% and 80% diamond (8 - 16 μm natural).

From Figure 4.21, it can be seen that as the diamond content increases, both the stiffness and strength increase, up to 75%, after which there is little change. This shows that the diamond-silicone bonding must be very good as the diamond has a significant reinforcing effect. The strength, and elongation to failure values for the 80% sample are compared to the quoted values for GE Silicone's high thermal conductivity material and the NuSil material in the Table 4.1 below. These materials are comparative high thermal conductivity materials which are silicone based, the significant difference being that they are filled with Boron Nitride and Aluminium Nitride fillers rather than diamond.

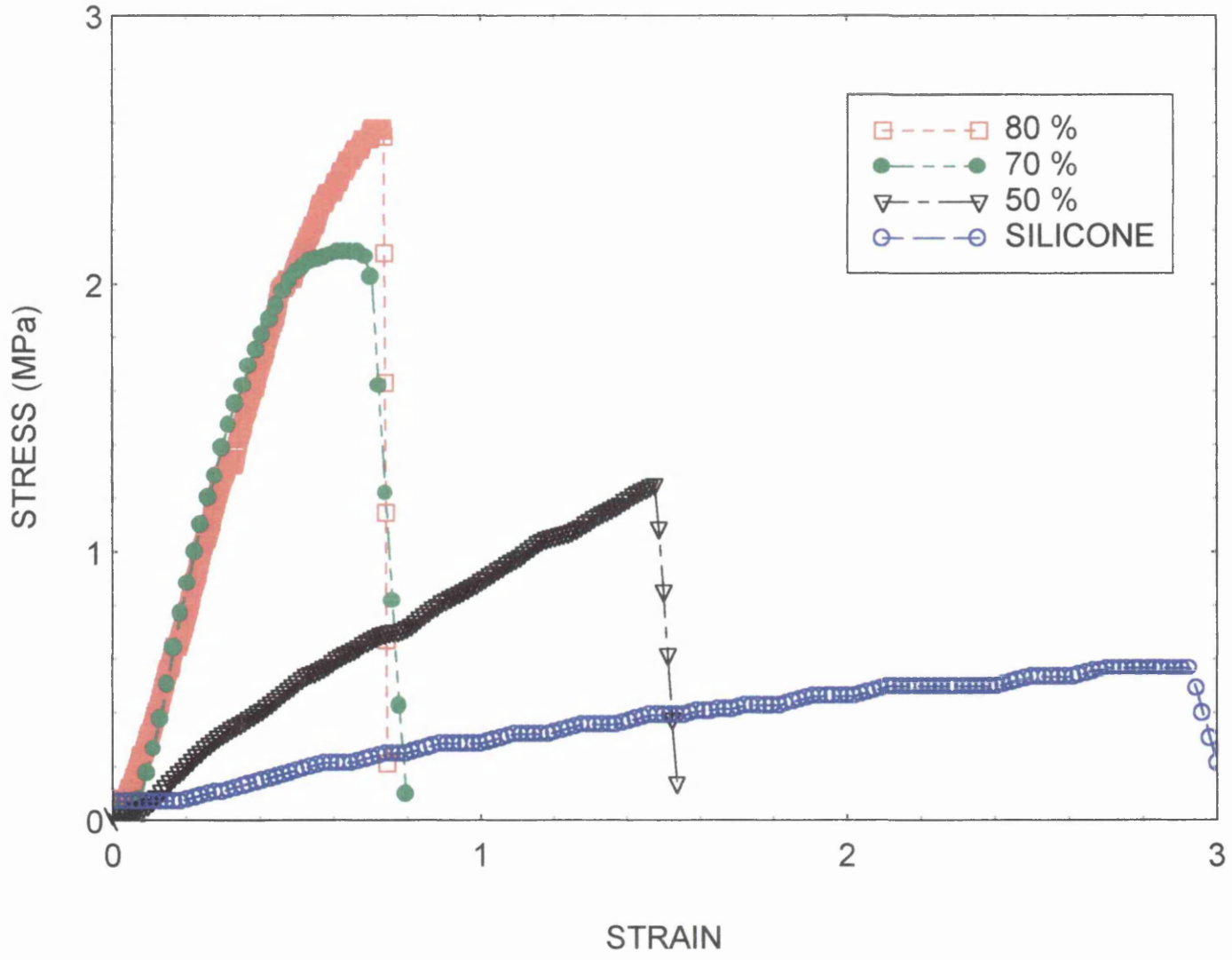


Figure 4.21 Tensile test results for an unfilled and three filled silicones.

Table 4.1 Mechanical properties of filled silicone materials

	80% Material	GE Material	NuSil Material
Strength (MPa)	2.2	4.5	1.7
Elongation (%)	70%	40%	75%
Thermal conductivity (W/mK)	2.4	1.68	1.46

4.3.7 DMTA Results

The DMTA tests were primarily performed to show how the stiffness varies across a wide temperature range. Figure 4.22 shows how the stiffness changes across the temperature range from -60°C to +100°C for an unfilled silicone and an 80% filled sample. From this it can be seen that the modulus is significantly higher for the 80 wt% material, but that otherwise the behaviour is similar. Both materials have a much higher modulus below about -40 °C, above which the value drops considerably. This region, normally termed the glass transition temperature, is at about the same temperature for both materials.

4.4 Conclusions

The optimum method of combining the diamond particles with a silicone polymer was found after much investigation. It was found that the combination of a flowable one part room temperature vulcanising silicone elastomer with small additions of solvent worked best to mix and cure with the diamond filler material. The best method of production was found to be that of combining the sample and rapidly compression moulding it, allowing curing to take place under pressure.

The methods of measurement of thermal conductivity were similarly refined until an optimal practice had been established.

A study of the effect of increasing the diamond filler content between 55 and 85% by weight, using natural diamond of the size range 8 - 16 μm, found that as the diamond content increased, and the porosity decreased, the thermal conductivity rose. For uniform

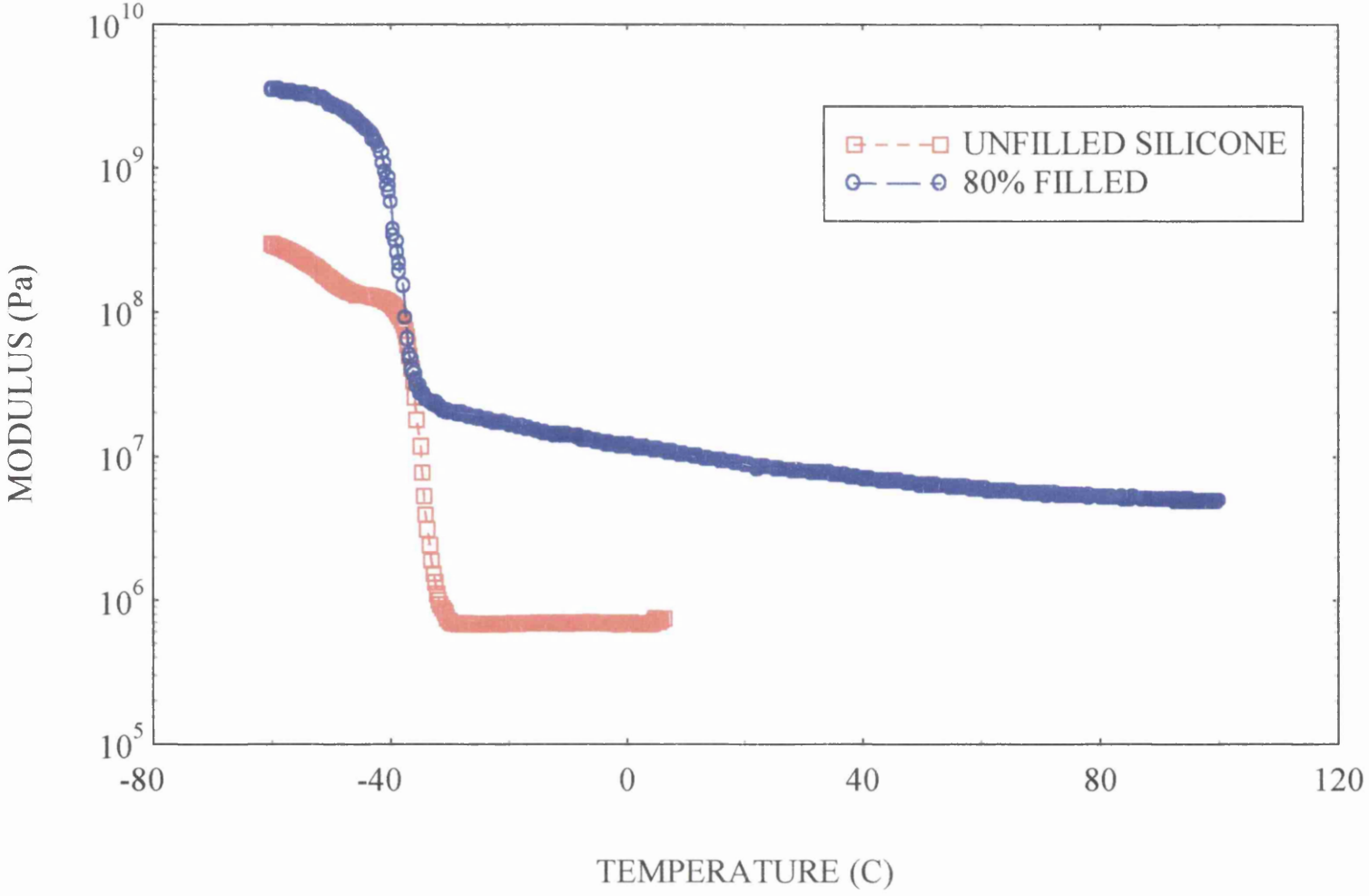


Figure 4.22 DMTA results for an unfilled and 80% filled silicone.

sized particles, the maximum amount that could be incorporated was 80% by weight diamond filler, which gave the thermal conductivity of about 2.3 W/mK. This compares to the value of 0.24 W/mK for unfilled silicone and a theoretical value of 2000 W/mK for diamond. A study of these samples was under taken using electron microscopy.

The size and type of the diamond particles had little effect other than that for sizes below 4 μm it was not possible to incorporate more than 70% by weight filler.

To achieve a filler loading of 85% by weight of diamond filler it was necessary to use a mix of diamond sizes, however this produced a thermal conductivity of 3.9 W/mK.

The diamond filler increased the thermal expansion of the material, which was unexpected as diamond on its own has a very low value. This was thought to be due to the entrapment of micro-pores as the expansion of these gas pockets will be higher than the surrounding material.

Increasing the diamond filler gave significant increases in strength and stiffness. The elongation to failure was decreased, but not significantly. This is probably due to the strong connection between the diamond particles and the silicone caused by the adsorbed water molecules on the diamond forming links with the curing silicone.

There was no observable effect on the temperature-dependence of stiffness, showing that the filled material has a similar usable temperature range to the unfilled material. The upper temperature limit was not investigated.

CHAPTER 5 DIAMOND FILLED POLYESTERS

5.1 Material

To investigate the effect of the body constituent material on the thermal conductivity of the composite further a few samples were produced using a two part, fast curing polyester resin. This material was mixed together to make the curing resin and the diamond was then measured and added to give the final composite. A mixture of different sized diamond particles was used as this had previously been found to be most effective at forming conductive networks in the earlier experiments on silicone based composites. Again it was found that the best method of production was compression moulding.

A variety of samples were made with the amount of filler ranging from 65% by weight to 80%. As the density of the material was different to that of the silicone it was necessary to recalculate the weight percent to volume percent ratio. The samples were calculated to range from 40 - 58% by volume fraction filler.

5.2 Testing

All the samples were tested using the thermal conductivity equipment described in section 3.1. These samples were sanded down using increasingly fine grades of paper to try and create as smooth a surface as possible and minimise the effect of the interfacial barrier. The thermal conductivity of an unfilled sample of polyester resin was also measured.

After the samples were tested for their thermal conductivity they were then compared under an optical microscope to assess the relative degree of porosity. This examination was necessary to judge the overall effect of porosity on the findings.

5.3 Results

The thermal conductivity of the unfilled sample of polyester resin was found to be 0.24 W/mK. The results for the filled samples are shown below in Figure 5.1. This shows the gradual increase of the thermal conductivity with the increase of the volume fraction of filler. The thermal conductivity rises from 0.64 W/mK at 40% filler to 1.43 W/mK when it was 58% filled. There is a small drop from 39.8 % filled by volume and 40.8% as the conductivity goes from 0.64 W/mK to 0.57 W/mK. All samples when studied under the microscope were found to have largely the same amount of micro-porosity.

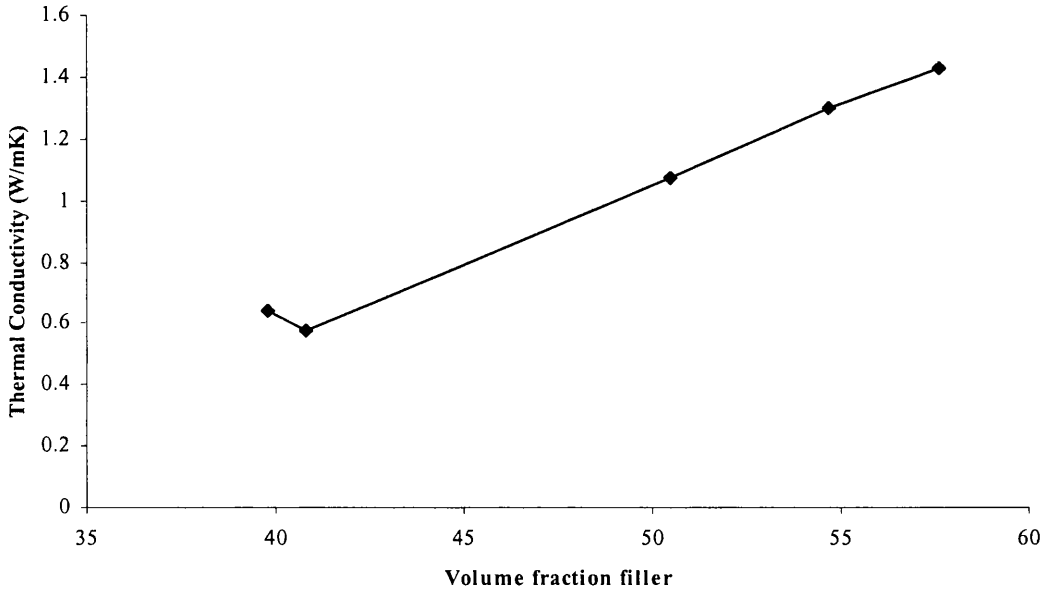


Figure 5.1 Graph of the effect of the volume fraction of diamond filler on the thermal conductivity of samples with a polyester matrix.

5.4 Conclusions

The thermal conductivity of diamond filled polyester was investigated and it was found that increasing the volume fraction filled from 40% to 58% increased the thermal conductivity from 0.64 W/mK to 1.434 W/mK.

It was expected that if the acoustic mismatch theory was correct then the polyester matrix, being substantially more rigid than that of the silicone based composites, would be more effective at transmitting the phonons through the material. If the theory were correct then the lower differential between the speed of sound in diamond and polyester than the differential between it in silicone and diamond would mean that there would be a far higher thermal conductivity for the polyester based material than previous theories would predict from merely the respective thermal conductivities. Whether the theory is incorrect or the differential between the speed of sound in polyester and diamond is simply too great to make a significant difference is difficult to gauge as it has been impossible to find comprehensive values for the relevant materials.

CHAPTER 6 DIAMOND FILLED PVC

6.1 Material

A mix of polyvinyl chloride and diamond was investigated. This was to discover if it was possible to create a heat conductive paint that would act as a protective and electrically insulating barrier, with reasonable heat dissipation properties. To this end pellets of polyvinyl chloride were measured out with diamond powder to establish the proportion of filler to matrix. It was found that the best percentage to give a compromise between the highest possible content of diamond and integrity of the final product was that of 81% diamond by weight or 67.5% by volume. Above this percentage there was insufficient polyvinyl chloride as a matrix to bind the diamond particles together and a material that was brittle and difficult to work with. At levels of filling less than this the diamond conductive networks were less extensive. The solvent used was tetrahydrafuran as this dissolved the polyvinyl chloride and then evaporated with virtually no trace left remaining. The filler used was a mixture of roughly 60-70% 15 μm diameter natural diamond with the remaining made up of 30-40% natural diamond of the size range 4-1 μm. This mixture was chosen as the most likely to form a high degree of packing and therefore a good continuous network throughout the material. The mixing of a random size distribution has been established as the best method by several papers (44,45) as the best to form continuous networks.

In order to build up a reasonable thickness of sample for testing, the material was painted onto the test surface in thin layers. These thin layers were then built up by allowing thorough drying of the previous before applying the next. This allowed a relatively uniform amount of material to be applied each time. It was found that with PVC samples it was extremely difficult to manufacture samples of high quality, low porosity, good mixing, etc by the same methods as previous samples. This was exacerbated by the extremely brittle nature of the unfilled poly(vinyl chloride) meaning that the compression needed to ensure good surface contact when measuring thermal conductivity would invariably break the sample. Poly(vinyl chloride) is also insoluble in most normal

solvents, the most effective solvents are those which appear to be capable of some form of interaction with the polymer.

When the solvent (tetrahydrafuran) was added the resultant solution was insufficiently viscous to suspend the larger particles of the diamond powder. This tended to lead to a degree of separation in the final sample with the larger particles settling to the bottom before the finer particles. Due to the highly volatile nature of the solvent the product also had a high degree of porosity and poor uniformity of final shape. It was therefore necessary to find a method of creating a usable sample and measuring the properties. Further, due to the low viscosity of the paint solution the diamond particles had a tendency to agglomerate when left to stand. This propensity to form clusters meant that when painted too thickly onto surfaces the solvent would re-dissolve the previous layers and form large clumps of diamond particles. These agglomerations would reduce the uniformity of the distribution of diamond particles and make it more difficult to measure the thermal conductivity as the surface would be very poor, raising the interfacial barrier. To create a more uniform surface from which to measure the heat loss, as an extremely rough surface would increase the surface area and lead to greater heat loss than would be predicted, the sample was lightly sanded after the final application.

6.2 Testing

Initial testing of this system was attempted as before, to measure the thermal conductivity through the material. Unfortunately this did not prove possible, mainly as it was impossible to obtain a sample with a uniform thickness greater than about half a millimetre. In addition, any potential application of such a paint would involve heat passing through the paint and then being lost to a free surface, rather than the material being sandwiched between two surfaces. Therefore, to test this paint in a meaningful way it was decided to carry out heat loss measurements where the heat was lost from the top surface by a radiative mechanism.

To do this, the heated half of the thermal conductivity measurement equipment was used to find how the amount of energy emitted varied with different coatings and thickness.

The equipment was set up so that a temperature gradient could be measured along the length of the insulated core from the heating element and the energy loss at the exposed face quantified. The heat input to the equipment was kept constant, and so a greater thermal barrier at the surface would have led to higher temperatures on the thermocouples. Readings were taken with a bare metal face, unfilled poly(vinyl chloride) coating and then the sample material in question. Figure 6.1 shows a typical temperature curve for a calibration test of an uncoated surface.

These tests were largely qualitative rather than quantitive as it is hard to exactly quantify the amount of energy lost through the sides of the equipment or the effect of the different forms of heat loss; convection and conduction to the surroundings. To minimise the effect of the cooling action of convection a tube was placed around the equipment. This tube was open ended and sufficiently large that it would not cause heat build up, it would however shield the equipment from any draughts.

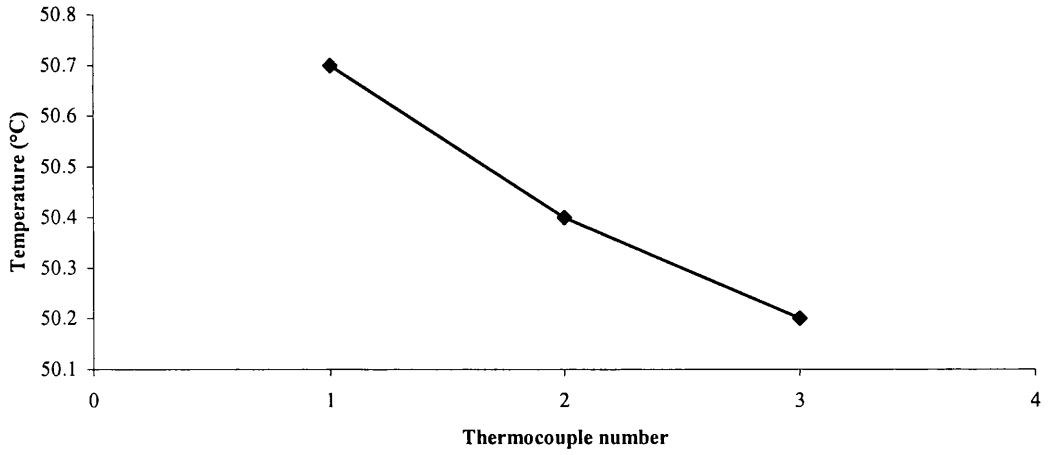


Figure 6.1 Variation of temperature along a heated bar with no covering at the exposed surface.

6.3 Results.

To establish some idea of the amount of energy radiated by the material under normal circumstances and to allow valid conclusions to be drawn from the results of the paint composites tests, some calibration experiments were carried out. Firstly, tests were carried out to find the temperature gradient along the bar without a surface coating. This established the base level of the radiation that would be emitted from the sample. It was assumed that as thermally insulating coatings were applied to the exposed surface the temperatures of the thermocouples would increase due to the additional insulation. When a layer of pure polyvinyl chloride dissolved in tetrahydrafuran was applied to an approximate thickness of 1.0 mm, the results were recorded and are shown below with the results of the uncoated tests in Figure 6.2. As can be seen from this figure the temperature loss was actually greater with the addition of the poly(vinyl chloride) coating. This initially surprising result is due to the altered radiative emissivity of the exposed end. As was discussed above the amount of radiation given off by a body is entirely determined by the emissivity of that object's surface. In this case it appears that the emissivity of the unfilled polyvinyl chloride was considerably higher than that of the bare copper metal.

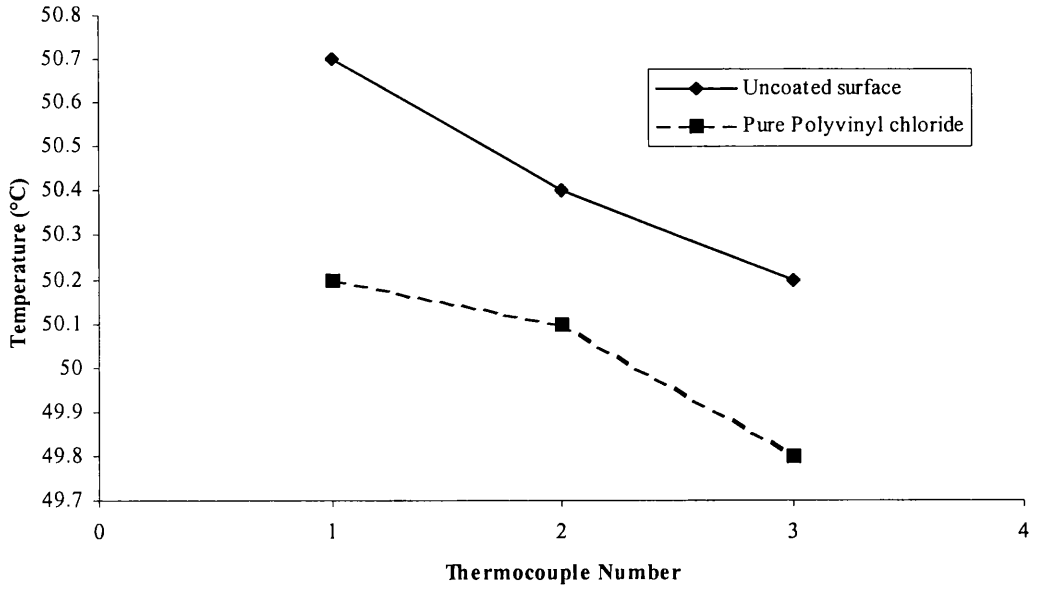


Figure 6.2 Comparison of the temperature gradient along a bar heated at one end with the opposing end firstly uncoated then coated with a layer of polyvinyl chloride.

The sample of filled polyvinyl chloride was then tested. The first sample tested was filled at 90% by weight (80% by volume) with diamond particles. It was only possible to place four coats of the sample material onto the equipment before the surface became unworkable, with large agglomerations of diamond particles causing an extremely uneven surface. It was not possible to sand the uneven surface of the 90% wt filed sample to a desirable evenness without causing it to break up. This high degree of brittleness was put down to there being insufficient amounts of body constituent material to bind the particles of diamond together. A variety of concentrations was then tried and the concentration that lent itself to the best compromise in filling and mechanical properties was 81 per cent by weight diamond filled or 67.5 per cent by volume. A reading of the temperature of the three thermocouples was taken after each layer of composite was painted on. It was necessary to leave a period of at least two hours after painting on a layer to allow the temperature to stabilise as the evaporation of the solvent caused the area to be cooled. The results of this are shown below in Figure 6.3. After the final readings were taken the sample was carefully peeled of the work piece and the thickness measured. The thickness of the material was found to be 2.43 mm. Assuming that when it had been sanded after the final layer was applied only one layer was removed that would mean the thickness of each layer was 2.43/12 = 0.20 mm per layer, on average.

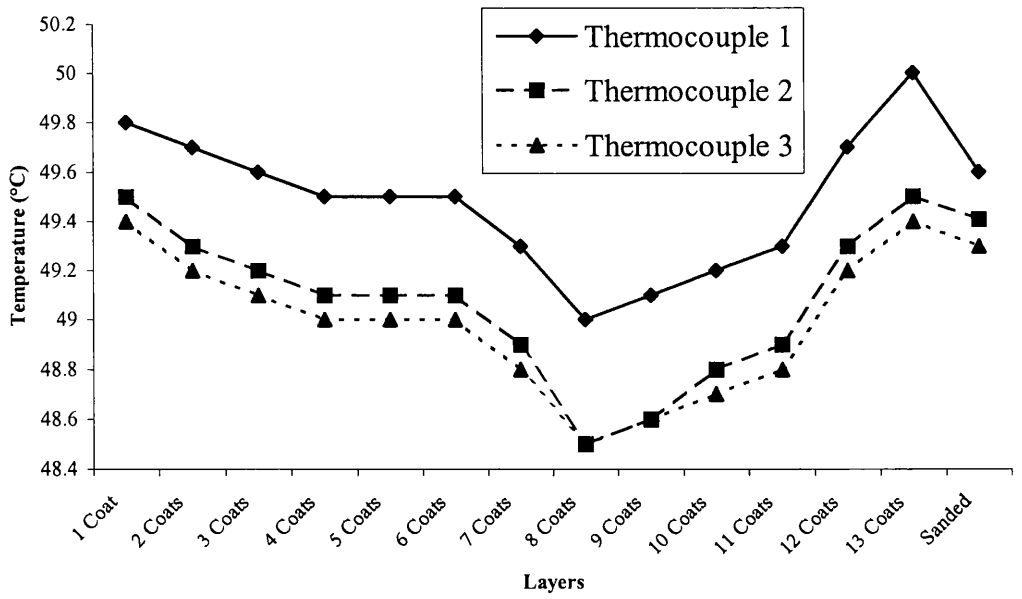


Figure 6.3 The change in temperature of the three thermocouples as additional layers of material are added.

From Figure 6.3, it can be seen that the thermocouple temperatures are lower than seen for either the uncoated case or for unfilled PVC. Additionally, the temperatures decreases as the number of coating layers increase, up to 8 layers, after which the temperatures rise again. The effect of sanding the final layer, and hence reducing thickness is seen as a reversal of this trend.

6.4 Discussion

It is clear from the results above that a thin layer of unfilled PVC allows greater heat loss from the system compared to the uncoated case. Further increases in heat loss are seen with a filled coating, up to a certain thickness, after which the heat loss decreases. It can be concluded that the initial drop in temperature with coating is related to the additional emissivity of the coating which allows more heat to be radiated away from the testing equipment. This emissivity is higher for non-metallic, darker and rougher surfaces, and so the increase in radiation from bare metal to uncoated PVC to filled PVC can be explained. The effect of greater heat loss as more filled material is added is probably due to a combination of a slightly rougher surface and lower porosity as more layers are added,

altering the emissivity and dispersing the heat more effectively. At the point when a thickness of 1.6 mm has been built up, the material is no longer able to effectively conduct the heat away from the equipment. At this point the rate determining step switches from that of the speed at which energy can be radiated from the surface, to the ability of the composite to conduct the material to the outer surface. As the layers build up it then becomes increasingly difficult for the material to conduct this heat to the outer surface and so the temperature rises.

CHAPTER 7 CONCLUSIONS AND FURTHER WORK

The best mix of diamonds was found to be that of mixing a variety of sizes of diamond particle to create a high degree of packing. By using a wide variety of particle sizes in the range between 2 μm and 16 μm in diameter it was found that materials incorporating filler of much higher concentrations could be made up. No real difference was found between using samples of natural and artificial diamond.

A variety of different types of silicone were experimented with and it was found that the best was a flowable one-part room temperature vulcanising silicone elastomer with small additions of solvent. It has been shown that the best method of producing samples of the silicone rubber composite material is by mixing the filler and matrix then compressing the material to minimise any voids present.

Investigations into the two-part polyester resin based composite showed there was the possibility of producing a material with very high thermal conductivity. Problems were highlighted with the mixing process that would need to be overcome. These deficiencies were the large amount of porosity that became locked into the composite due to the high viscosity of the setting material and conversely the problem of mixed material settling were it is left to stand before setting.

The poly vinyl chloride based composite showed a large increase in the amount of heat radiated. This demonstrates the ability of the material to transmit and radiate heat effectively. It is hoped that with some further work to perfect the application and mixing of the material a very effective material can be produced.

It has been shown that the largest obstacle to increased performance in the composite is lack of a continuous conductive path through the material and the presence of voids. To increase the likelihood of a continuous conductive path through the materials it is necessary to load the largest amount of filler possible without losing the physical characteristics of the material. It would be desirable to find the best mix of diamond sixes to use as filling material and there is still work to be done in this area.

Although compression moulding the samples was found to be most effective at minimising the voids present in the material they did not eliminate them entirely. The avenue of placing the material under a vacuum to release any pores of gas incorporated before moulding also seem a promising avenue of exploration.

Much work has been devoted to studying the optimisation of the thermal conductivity. While some tests have been carried out to determine the thermal expansion, temperature dependence of stiffness, elongation to failure and strength of the silicone elastomer based composite, a more comprehensive study of the physical properties is needed.

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